The Purple Pigments produced by Acetylation of 2-(2-Oxoindolin-3-yl)-glyoxylates in the Presence of Pyridine

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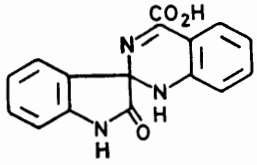
The reaction of 2-(2-oxoindolin-3-yl)glyoxylates with acetic anhydride in the presence of pyridine gives insoluble purple pigments in which two molecules of the indoline have condensed with one molecule of acetic anhydride and for which a spirocyclobutene structure (13a) is suggested. The mode of formation of the pigments is discussed.

THE chemistry of oxoindolines abounds with examples of complex pigmented products being produced under unexpected circumstances. Treatment of isatin with ammonia yields the red isamic acid [1] (1) and the reaction of *O*-methylisatin with moist acetic acid produces the orange methylisatoid [1] (2). Simply dissolving indoxyl in organic solvents affords the blue indigotin [2] (3). The attempted base-catalysed acylation of isatin with acetic anhydride gives the purple pigment [3] (4) and with propionic anhydride the red-brown pigment [4] (5) is obtained.



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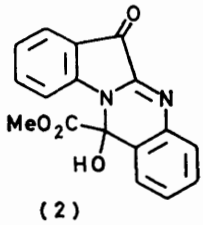

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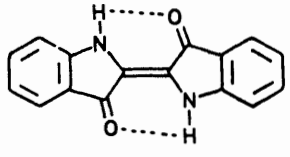

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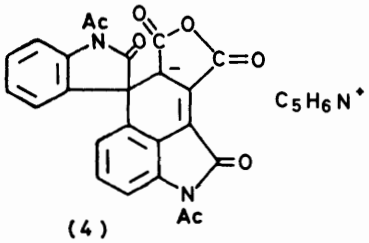

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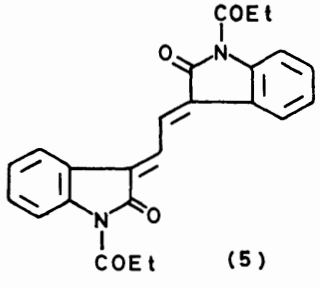

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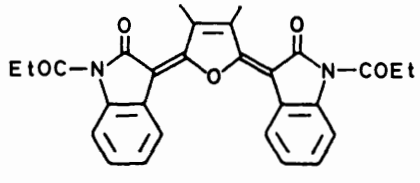


(6)

The red-brown pigment [5] (6) formed by treatment of ethyl 2-(2-oxoindolin-3-yl)glyoxylate [6] (7; R = Et) with propionic anhydride and pyridine further illustrates

[1] J. W. Cornforth, *J.C.S. Perkin I*, 1976, 2004.
[2] G. A. Russell and G. Kaupp, *J. Amer. Chem. Soc.*, 1969, **91**, 3851.
[3] J. A. Ballantine, A. W. Johnson, and A. S. Katner, *J. Chem. Soc.*, 1964, 3323.
[4] A. W. Johnson and A. S. Katner, *J. Chem. Soc.*, 1965, 1455.
[5] M. Alam and J. A. Ballantine, *J. Chem. Soc.* (*C*), 1968, 255.
[6] L. Horner, *Annalen*, 1941, **548**, 117.

the remarkable facility of these compounds for forming conjugated chains, even in this case making use of air in an oxidation step.

In a continued examination of this phenomenon, methyl 2-(2-oxoindolin-3-yl)glyoxylate (7; R = Me) has been treated with acetic anhydride and pyridine to yield a purple crystalline pigment with a dark green reflex. Microanalysis and mass spectrometry established the molecular formula $C_{25}H_{18}N_2O_6$. The presence of an intact ester function was inferred when similar pigments were obtained from the ethyl and benzyl esters of the starting material, each fitting the general formula $C_{23}H_{15}N_2O_4 + CO_2R$ and having identical visible spectra. The presence of two nitrogen atoms suggested that two molecules of the starting material had participated in the reaction but only one ester function remained in the product. The i.r. spectra of the pigments (Table 1)

TABLE 1

I.r. carbonyl absorptions of the pigments and related compound (ν/cm^{-1})

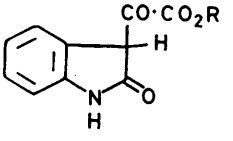
Methyl ester pigment (13a)	1 731, 1 725, 1 705, 1 690
Methyl leuco-compound	1 740, 1 710, 1 645
Reduced methyl leuco compound (14)	1 750, 1 705
Oxidation product (A) (12a)	1 790, 1 775, 1 767, 1 725, 1 650
Methanolysis product (B) (10; R = H)	1 720, 1 670
N-Acetylindolin-2-one	1 760, 1 695
N-Acetylisatin	1 783, 1 745, 1 710

showed no absorptions in the OH or NH regions but exhibited strong carbonyl absorptions reminiscent of *N*-acetyl-2-oxoindolin-3-yl derivatives. The ^{1}H n.m.r. spectrum of the more soluble methyl ester pigment (Table 2) showed absorptions consistent with the presence of two non-equivalent *N*-acetyl-2-oxoindolin-3-yl systems in addition to the methyl ester function. The remaining proton gave rise to a sharp low-field singlet, and the spectral evidence could be summarised in terms of the partial stucture (8). Written in this way the extraordinary degree of unsaturation which must be present in the central linking portion of the molecule can readily be appreciated.

Treatment of the methyl ester pigment with chromium trioxide in acetic acid yielded two crystalline oxidation products. One was obtained as light yellow needles, $C_{10}H_7NO_3$, the spectroscopic properties of which established its identity as *N*-acetylisatin (*cf.* ref. 5).

The second oxidation product, designated (A), was obtained as colourless needles, $C_{15}H_{11}NO_6$, which had a u.v. spectrum with some similarity to that of *N*-acetylindolin-2-one. These two oxidation products together accounted for all of the carbon, hydrogen, and nitrogen atoms present in the original pigment and must have arisen from oxidative fission of the material into two with addition of three oxygen atoms.

The i.r. spectrum of (A) (Table 1) had no OH or NH absorptions but had a very complex carbonyl absorption region indicating the presence of a number of carbonyl functions. The ^{1}H n.m.r. spectrum (Table 2) was consistent with the presence of an *N*-acetyl-2-oxoindolin-3-yl system, a methyl ester function, and a single isolated olefinic hydrogen atom. The spectral evidence for (A) could therefore be summarised in terms of the partial structure (9), and it seemed probable that the extra



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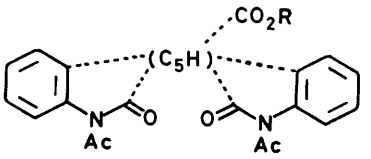

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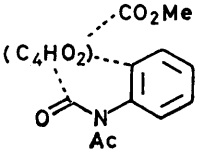

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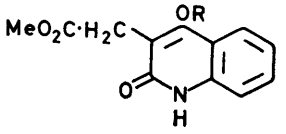


(10)

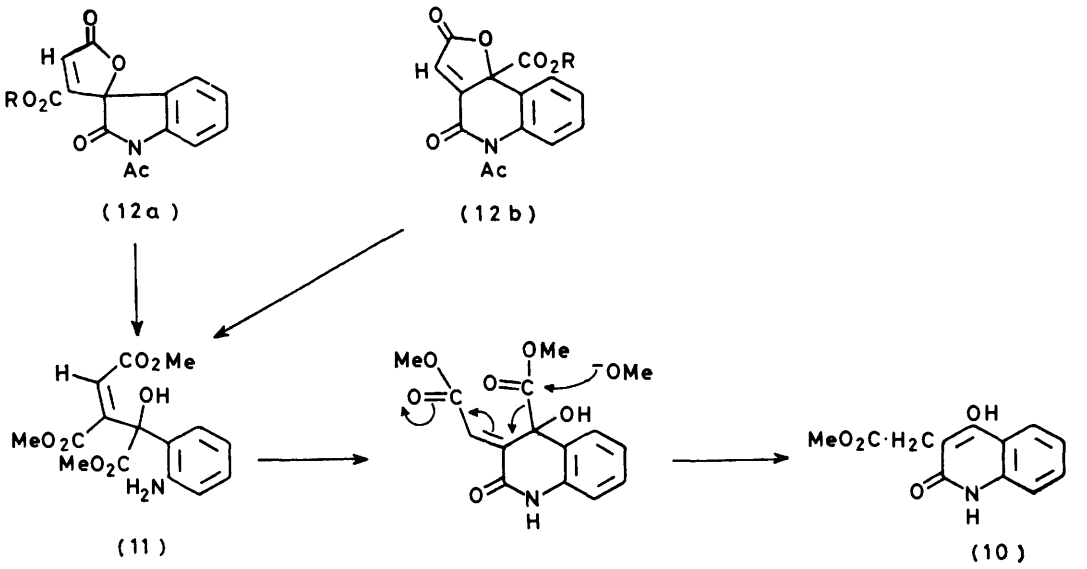
oxygen atoms were present in a lactone function. Accordingly (A) was treated with sodium methoxide to yield a crystalline methanolysis product, $C_{12}H_{11}NO_4$ [designated (B)] which had lost one ester function as well as to the *N*-acetyl group. The mass, i.r., u.v., and ^{1}H n.m.r. spectral data suggested that (B) might be a 4-hydroxyquinolone derivative, and on treatment with ethereal diazomethane a methyl ether was obtained which was identical with synthetic methyl 1,2-dihydro-4-methoxy-2-oxoquinoline-3-acetate [7] (10; R = Me). The structure of the degradation product (B) was therefore established as (10; R = H). When the ethyl or benzyl ester analogue of (A) was treated with methoxide ion an identical (B) *methyl* ester was obtained.

The relationship of the methanolysis product (B) to the original lactone (A) is complex, involving opening and deacetylation of the *N*-acetylimide system, opening of the lactone ring, ring closure of the open 2-oxoindolin-3-ylacetic acid system to the preferred quinoline ring,[8] and expulsion of the ester function. The intermediate ring-opened material may be written as (11), in which the ester function is present as a vinylogous β-diester, thus permitting a ready retro-Claisen ester reaction as shown in Scheme 1. The foregoing evidence permits only two rational lactone structures for (A), and these are represented by (12a and b), both of which are consistent with both the spectral data and the chemical evidence. Two alternative structures containing β-lactone ring sytems are theoretically possible for (A), but are considered unlikely for a variety of reasons.

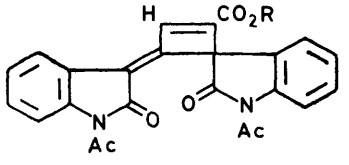
The presence of a benzylic lactone function in (A) was confirmed by catalytic hydrogenation: the ring was hydrogenolysed to give a tetrahydro-carboxylic acid [9] derivative.

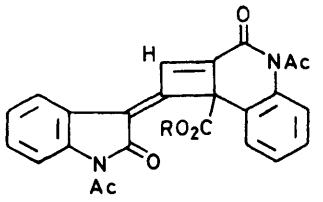
[7] T. A. Geissman and A. K. Cho, *J. Org. Chem.*, 1959, **24**, 41.
[8] J. A. Aeschlimann, *J. Chem. Soc.*, 1926, 2902.
[9] R. Filler, E. J. Piasek, and L. H. Mark, *J. Org. Chem.*, 1961, **26**, 2659.

The oxidation of the methyl ester pigment to (A) seemed at this stage to involve the oxidative cleavage of the indolin-3-ylidene double bond to give two ketonic fragments, followed by insertion of the lactone oxygen atom into what must be a cyclobutenone system to give an αβ-unsaturated γ-lactone. This is an unusual reaction bearing general similarities both to the Baeyer–Villiger oxidation of ketones by peroxides [10] and to the production of the bicyclic tetrahydrofuran system in pinol by 'oxidation' of the cyclobutane ring in α-pinene.[11]



SCHEME 1





These conclusion lead to two alternative cyclobutene structures for the methyl ester pigments (13a and b) (R = Me), both of which are capable of existing in two geometrical isomeric forms, each of which would also be a racemate.

Confirmation of the presence of the cyclobutene ring system in the methyl ester pigment was obtained by reduction. Treatment with zinc in acetic acid gave a colourless dihydro-product which could easily be oxidised back to the original pigment by refluxing in a solvent containing dissolved air, or very rapidly by addition of animal charcoal. The ^{1}H n.m.r. spectrum of this leuco-compound (Table 2) had lost the low field olefinic proton signal, which had been replaced by an AMX system with very characteristic coupling constants of 16.3, 6.5, and 3.5 Hz. These values are in the exact range found for geminal and vicinal couplings in cyclobutane systems when the geminal protons are adjacent to a π-system,[12] and are well outside the range found for cyclopropane systems. The non-equivalence of the *N*-acetyl absorptions and the u.v. absorption confirm that the indolin-3-ylidene double bond is still intact in the leuco-compound, and that reduction has taken place in the cyclobutene ring exclusively.

Cleavage of the cyclobutene ring takes place under hydrogenation conditions [13] when the leuco-compound is hydrogenated over palladium to produce a colourless hexahydro-derivative of the pigment. The ^{1}H n.m.r. spectrum of the hexahydro-derivative was complicated by stereoisomerism (the product, containing three chiral centres, could be a mixture of eight diastereoisomers), but clearly indicated that the benzenoid systems were intact, that no terminal methyl group had been produced, and that the two *N*-acetyl systems were now equivalent. The u.v. spectrum of the hexahydro-product was very similar to that of *N*-acetylindolin-2-one and the product can probably be formulated as (14a or b) (R = Me).

Any proposed structure for the pigments must be capable of explaining the visible spectra of the materials, and both the proposed structures can accommodate the observed purple colour of the solutions. A charged

[10] C. H. Hassall, *Org. Reactions*, 1957, **9**, 73.
[11] S. S. Nametkin and A. G. Yartzeva, *J. Russ. Phys. Chem. Soc.*, 1924, **55**, 521.
[12] A. A. Bothner-By, *Adv. Magnetic Resonance*, 1965, **1**, 195.
[13] J. Newham, *Chem. Rev.*, 1963, **63**, 123.

enolate anion–ammonium ion form of (13b) would have a complete conjugated π-system incorporating both indole rings which could explain the colour. The molecule (13a) should be capable of exhibiting spiroconjugation [14] of rational formation by the mechanism presented in Scheme 2. Acetylation of the nitrogen atom and the reactive carbanion would result in the production of (15), which would react with another molecule of

TABLE 2

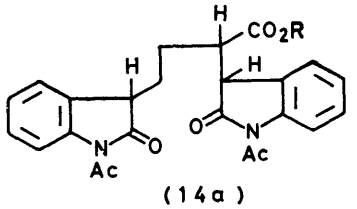
^{1}H N.m.r. spectral data for the pigments and related compounds [τ ($CDCl_3$); J in Hz]

	Olefinic	Aromatic	CO_2Me	NAc	Aliphatic
Methyl ester pigment (13a)	1.20 (1 H, s)	1.70 (3 H, m), 2.10 (1 H, m), 2.70 (4 H, m)	5.92 (3 H, s)	7.02 (3 H, s), 7.22 (3 H, s)	
Methyl leuco-compound		1.84 (3 H, m), 2.56 (1 H, m), 2.78 (4 H, m)	6.36 (3 H, s)	7.18 (3 H, s), 7.30 (3 H, s)	5.16 (1 H, dd J 16.3 and 3.5), 5.99 (1 H, dd, J 3.5 and 6.5), 6.88 (1 H, dd J 6.5 and 16.3)
Reduced methyl leuco-compound (14)		1.62br (2 H, d), 2.66br (6 H, m)	6.41 (3 H, s)	7.3 (6 H, s)	6.01 (1 H, t), 6.30br (1 H, m), 6.7 (1 H, m), 7.9br (4 H, m)
Oxidation product (A) (12a)	3.08 (1 H, s)	1.7 (1 H, d), 2.58 (1 H, m), 2.85 (2 H, m)	6.29 (3 H, s)	7.33 (3 H, s)	
Methanolysis product (B) (10; R = H) *		1.7 (1 H, d), 2.15 (3 H, m)	6.0 (3 H, s)		5.85 (2 H, s)
N-Acetylindolin-2-one		1.6br (1 H, m), 2.65br (3 H, m)		7.32 (3 H, s)	6.28 (2 H, s)
N-Acetylisatin †		1.8 (1 H, d), 2.30 (2 H, m), 2.7 (1 H, t)		7.48 (3 H, s)	

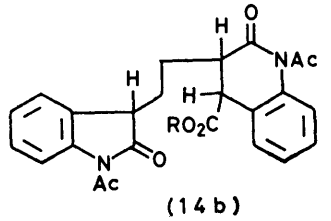
* In trifluoroacetic acid. † In [$^2H_6$]dimethyl sulphoxide.

similar to that observed in isamic acid [1] (1) and the purple pigment [3] (4), which should result in a deep colouration.

Differentiation between the two structures was attempted by considering the possible mechanism



(14a)



(14b)

of formation of the pigment from the starting material (8). The ester function in the pigment must arise from the 2-oxoindolin-3-yl reactant, in which the ester is two carbon atoms removed from the benzene ring. However, in the structure represented by (13b), the ester function is one carbon atom removed from one benzene ring and three carbon atoms removed from the other. Such a situation could only occur as the result of extensive rearrangement of an unknown type.

The molecule represented by (13a), however, is capable of rational formation by the mechanism presented in Scheme 2. Acetylation of the nitrogen atom and the reactive carbanion would result in the production of (15), which would react with another molecule of *N*-acetyl-2-oxoindolin-3-yl carbanion to furnish compound (17), perhaps through the intermediacy of (16), which has been isolated from the reaction mixture. The elimination of the glyoxylic ester function is simply a base-catalysed retro-Claisen ester reaction (' acid fission '). The methyl group in (17) is very reactive as it is both a vinylogous active methyl group and a vinylogous benzylic function similar to that postulated as an intermediate during the formation of (6).[5] Claisen condensation of this active carbanion centre with the neighbouring oxo-group followed by base-catalysed dehydration would furnish the cyclobutene ring system of (13a).

As a rational mechanism for the production of the alternative stucture (13b) is not available, structure (13a) is preferred for the ethyl ester pigment.

EXPERIMENTAL

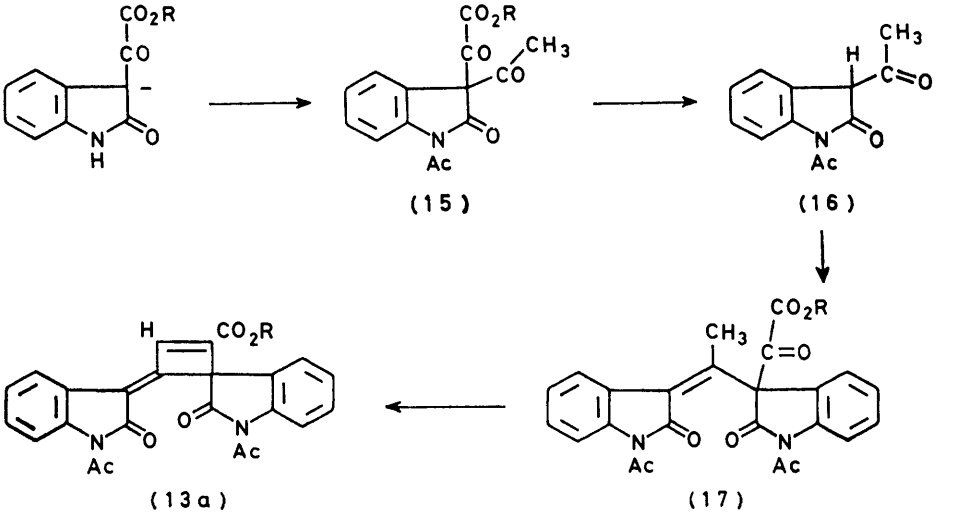
I.r. spectra were measured for KBr discs; silica used for column chromatography was acid washed 200—300 mesh (Koch–Light).

Methyl 2-(2-Oxoindolin-3-yl)glyoxylate (7; R = Me).—Dimethyl oxalate (39 g) was condensed with indolin-2-one (30 g) in the usual way [6] to give the *glyoxylate* as yellow needles (26.5 g), m.p. 160—163° (Found: C, 60.1; H, 4.3; N, 6.6%; M^+, 219. $C_{11}H_9NO_4$ requires C, 60.3; H, 4.1; N, 6.4%; M, 219).

Methyl 1′-Acetyl-4-(1-acetyl-2-oxoindolin-3-ylidene)-2′-oxospiro[cyclobut-2-ene-1,3′-indoline]-2-carboxylate (13a; R = Me) Methyl 2-(2-oxoindolin-3-yl)glyoxylate (10 g) was refluxed with acetic anhydride (20 ml) and pyridine (10 ml) for 30 min, then the product was set aside to crystallise. After 14 days the crystals were collected and washed with acetone; the crude product (3.6 g) was recrystallised from acetic anhydride to give the *methyl ester pigment* as small dark needles

[14] H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, 1967, **89**, 5208.

with a green reflex, m.p. 252—245° (decomp.) (Found: C, 68.3; H, 4.2; N, 6.4. $C_{25}H_{18}N_2O_6$ requires C, 67.9; H, 4.1; N, 6.3%), $\lambda_{max.}$ (dioxan) 245 ($10^4\varepsilon$ 2.34), 267(1.76), 340 (0.85), 364sh (0.74), 520 (1.47), and 538 nm (1.54), *m/e* 442(6%), M^+, 400(80, M − 42), 358(100, M − 42 − 42), 298(35), 270(22), 242(13), 72(22), 43(62), and 42(69).



SCHEME 2

The filtrate and acetone washings were combined and concentrated to small bulk. The resultant solid was collected and chromatographed by gradient elution on a silica column. One fraction contained 1,3-diacetylindolin-2-one (53 mg), obtained as colourless needles (from light petroleum), m.p. 108—109°, identical with an authentic sample prepared by *N*-acetylation of 3-acetylindolin-2-one.[15]

Ethyl 2-(2-oxoindolin-3-yl)glyoxylate [6] (8 g) was treated in a similar way with acetic anhydride and pyridine to yield the *ethyl ester pigment* (13a; R = Et) (2.95 g), m.p. 240—242° (decomp.) (Found: C, 68.4; H, 4.6; N, 6.0. $C_{26}H_{20}N_2O_6$ requires C, 68.4; H, 4.4; N, 6.1%), *m/e* 456-(5%, M^+), 414(91, M − 42), 372(87, M − 42 − 42), 298(16), 270(9), 242(13), 43(100), and 42(51).

Benzyl 2-(2-oxo-3-indolyl)glyoxylate [16] (8 g) under identical conditions yielded the *benzyl ester pigment* (13a; R = CH_2Ph) (1.87 g), m.p. 239° (decomp.) (Found: C, 72.1; H, 4.5; N, 5.6. $C_{31}H_{22}N_2O_6$ requires C, 71.8; H, 4.3; N, 5.4%).

Oxidation of the Pigments.—The methyl ester pigment (10 g) was suspended in acetic acid (400 ml) and a solution containing chromic oxide (14 g), water (10 ml), and acetic acid (150 ml) was added gradually to the stirred suspension at room temperature during 30 min. After stirring for a further 30 min, the solution was evaporated to dryness under reduced pressure. The residue was partitioned between water and ether, the ether layer dried, and the solvent removed. The crude product (7.0 g) was dissolved in benzene and applied to a silica column; gradient elution gave a number of fractions.

Early fractions deposited a yellow solid which on recrystallisation from ethyl acetate–light petroleum yielded *N*-acetylisatin as lime yellow needles (1.48 g), m.p. 141° (Found: C, 63.8; H, 4.0. Calc. for $C_{10}H_7NO_3$: C, 63.5; H, 3.7%), identical (i.r., n.m.r., u.v., and mass spectra and mixed m.p.) with a synthetic sample.[17]

Later fractions deposited a colourless solid which was recrystallised from ethyl acetate–light petroleum to yield *methyl 1'-acetyl-2',5-dioxospiro[furan-2(5H),3'-indoline]-3-carboxylate* (12a; R = Me) as prisms (1.98 g), m.p. 152—153° (Found: C, 59.8; H, 3.4; N, 4.7. $C_{15}H_{11}NO_6$ requires C, 59.8; H, 3.7; N, 4.7%), *m/e* 301(8%, M^+), 259(100, M − 42), 231(3, M − 42 − 28), 227(8, M − 42 − 32), 183(11), 146(32), 90(15), and 43(81).

Other fractions contained *N*-acetylanthranilic acid [18] and 2-(acetylamino)phenylglyoxylic acid,[19] identical with authentic samples

The ethyl ester pigment (10 g) under identical oxidation conditions yielded *N*-acetylisatin (2.3 g) and the *ethyl spiro-[furan-2(5H),3'-indoline]carboxylate* (12a; R = Et) (2.1 g), m.p. 96—98° (Found: C, 61.1; H, 4.4; N, 4.3; M^+, 315. $C_{16}H_{13}NO_6$ requires C, 61.0; H, 4.2; N, 4.4%; M, 315).

The benzyl ester pigment (4 g) under identical conditions yielded *N*-acetylisatin (800 mg) and the *benzyl ester* (12a; R = CH_2Ph) (700 mg), m.p. 132° (Found: C, 66.9; H, 4.3; N, 3.3%; M^+, 377. $C_{21}H_{15}NO_6$ requires C, 66.9; H, 4.0; N, 3.7%; M, 377).

Methanolysis of the Lactones (12a).—The methyl ester (12a; R = Me) (4 g) was refluxed with sodium methoxide [from sodium (5 g)] in anhydrous methanol (200 ml) for 8 h. The solution was cooled, acidified with dilute hydrochloric acid, and extracted with ethyl acetate. The residue from the organic layer was recrystallised from ethyl acetate to yield *methyl 1,2-dihydro-4-hydroxy-2-oxoquinoline-3-acetate* as colourless needles (1.9 g), m.p. 210° (decomp.) (Found: C, 61.9; H, 5.1; N, 6.4%; M^+, 233.0678 ± 0.0012. $C_{12}H_{11}NO_4$ requires C, 61.8; H, 4.8; N, 6.0%; M, 233.0678), $\lambda_{max.}$ (MeOH) 229 ($\varepsilon \times 10^4$ 2.2), 306(0.96), and 318 nm (0.87).

The ethyl and benzyl ester (12a) also yielded (10; R = H) under identical methanolysis conditions.

Hydrogenolysis of the Lactone (12a; R = Me).—The methyl ester (12a; R = Me) (500 mg) was dissolved in methanol (200 ml) and hydrogenated at atmospheric pressure for 36 h over palladium–carbon (10%; 75 mg). *1-Methyl hydrogen 2-(1-acetyl-2-oxoindolin-3-yl)succinate* was

[15] H. Kondo, T. Nozoye, and M. Tobita, *Ann. Reports I.T.S.U.U. Lab.*, 1952, **3**, 70.
[16] P. L. Julian, H. C. Printy, R. Ketcham, and R. Doone, *J. Amer. Chem. Soc.*, 1953, **75**, 5305.
[17] C. Libermann and R. Kraus, *Ber.*, 1907, **40**, 2492.
[18] P. P. Bedson and A. J. King, *J. Chem. Soc.*, 1880, **37**, 753.
[19] Camps, *Arch. Pharm.*, 1899, **237**, 687.

crystallised from ethyl acetate–light petroleum to furnish colourless prisms (385 mg), m.p. 156—158° (Found: C, 58.8; H, 5.1; N, 4.7. $C_{15}H_{15}NO_6$ requires C, 59.0; H, 5.0; N, 4.6%), $\nu_{max.}$ 2 500—3 500br (CO_2H), 1 750, and 1 715 cm^{-1}.

Treatment of the Hydroxyquinoline (10; R = H) *with Diazomethane*.—Treatment of the hydroxyquinoline (300 mg) with ethereal diazomethane produced the *methyl ether* as colourless needles (from methanol) (270 mg), m.p. 181—182° (Found: C, 63.0; H, 5.4; N, 5.6. $C_{13}H_{13}NO_4$ requires C, 63.2; H, 5.3; N, 5.7%); $\nu_{max.}$ 1 730 and 1 660 cm^{-1}; $\lambda_{max.}$ (MeOH) 235 ($\varepsilon \times 10^4$ 1.35), 245sh (0.93), 262sh (0.52), 270(0.39), 278 (0.38), 313sh (0.50), 324 (0.39), and 339 nm (0.37), τ ($CDCl_3$) 2.3 (1 H, m, ArH), 2.6 (2 H, m, ArH), 2.8 (1 H, m, ArH), 6.02 (3 H, s, OMe), 6.25 (2 H, s, CH_2), and 6.28 (3 H, s, CO_2Me), identical (i.r., n.m.r., u.v., and mass spectra and mixed m.p.) with a synthetic sample [7,20] prepared by the method of Geissman.

Reduction of the Methyl Ester Pigment with Zinc and Acetic Acid.—The methyl ester pigment (4 g) was suspended in acetic acid (300 ml) and stirred at 100 °C during the gradual addition of zinc dust (5 g) over 1 h while the purple colour gradually disappeared. Insoluble materials were removed and the filtrate was evaporated to dryness under reduced pressure. The resulting light pink solid was extracted with water to remove inorganic salts; the residue (1.3 g) was dissolved in benzene and subjected to gradient elution on a column of silica gel. Intermediate fractions yielded the *methyl leuco-compound*, which was obtained as colourless prisms (from chloroform–light petroleum) (1.05 g), m.p. 210° (decomp.) (Found: C, 68.0; H, 4.6; N, 6.35%; M^+, 444. $C_{25}H_{20}N_2O_6$ requires C, 67.6; H, 4.5; N, 6.3%; M, 444), $\lambda_{max.}$ (dioxan) 267 ($\varepsilon \times 10^4$, 1.05), 293 (0.86), 315 (0.79), and 354 nm (1.30).

Oxidation of the Methyl Leuco-compound in Air.—The methyl leuco-compound (1 g) was refluxed with acetic anhydride (85 ml) and animal charcoal (100 mg) for 30 min. The hot purple solution was filtered and set aside to crystallise. Purple needles (114 mg), m.p. 252° (decomp.) were deposited which were identical with the methyl purple pigment (Found: C, 67.8; H, 3.9. Calc. for $C_{25}H_{18}N_2O_6$: C, 67.9; H, 4.1%).

Hydrogenation of the Methyl Leuco-compound.—The methyl ester leuco-compound (1.5 g) was hydrogenated in methanol (150 ml) over palladium–carbon (10%; 150 mg) at atmospheric pressure for 18 h. On removal of catalyst and solvent the reduced methyl leuco-compound was obtained as colourless prisms (from light petroleum) (900 mg), m.p. 58—60° (Found: C, 67.3; H, 5.6; N, 6.0%; M^+, 448. Calc. for $C_{25}H_{24}N_2O_6$: C, 66.9; H, 5.4; N, 6.3%; M, 448); $\lambda_{max.}$ (MeOH) 214sh ($\varepsilon \times 10^4$ 1.45), 233 (1.19), 255sh (0.58) and 278sh nm (0.20) [*cf.* $\lambda_{max.}$ (MeOH) for *N*-acetylindolin-2-one: 214sh (0.99), 233 (1.19), 255sh (0.42), and 278sh (0.12)].

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