Studies on the Syntheses of Heterocyclic Compounds. Part 738. † Photo-oxygenation of 9-Oxo-9*H*-pyrrolo[1,2-*a*]indoles

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Photo-oxygenation in methanol of 7-methoxy-6-methyl-9-oxo-9*H*-pyrrolo[1,2-*a*]indole (10), prepared from 2-bromo-5-methoxy-4-methylbenzaldehyde (5) *via* 2-(2-bromo-5-methoxy-4-methylbenzoyl)pyrrole (8), formed (±)-9,9a-dihydro-3α-hydroperoxy-9-oxo-7,9aβ-dimethoxy-6-methyl-3*H*-pyrrolo[1,2-*a*]indole (14) and the (±)-3α-hydroxy-compound (16). The corresponding 9a-ethoxy- (20) and 9a-isopropyloxy-derivatives (21) were obtained from the photo-oxygenation of compound (10) in ethanol and isopropyl alcohol, respectively. The dye-sensitized photo-oxygenation of 9-oxo-6,7-dimethoxy-9*H*-pyrrolo[1,2-*a*]indole (11) was also carried out in methanol.

THE mitomycins (1) are a family of antibiotics which possess activity against both gram-positive and -negative bacteria but are more noted for their antitumour properties. The introduction of the oxo-substituent at the C-9a position seems to be one of the most difficult problems in the synthesis of mitomycins. Elimination of 9a-hydroxy- or methoxy-group occurs very easily under a mild acidic treatment.[1-3] but the introduction of an oxo-substituent at this position has been reported. Attempted photo-oxidation of the 9*H*-pyrrolo[1,2-*a*]-indoles (2) gave only dehydrated products (3) [4,5] and 9-oxo-9*H*-pyrrolo[1,2-*a*]indole (4) failed to react with singlet oxygen.[4] Since we expected that the presence of electron-donating groups on ring A would activate the addition of singlet oxygen to the pyrrole ring C in 9-oxo-9*H*-pyrrolo[1,2-*a*]indoles, we prepared 6,7-disubstituted 9-oxo-9*H*-pyrrolo[1,2-*a*]indoles and subjected them to dye-sensitised photo-oxygenation. Here we report the formation of the 9aβ-alkoxy-3α-hydroxy-9,9a-dihydro-3*H*-pyrrolo[1,2-*a*]indoles and the corresponding 3-hydroperoxy-derivatives.

The synthesis of 6,7-disubstituted 9-oxo-9*H*-pyrrolo-[1,2-*a*]indoles was carried out as follows. Oxidation of 2-bromo-5-methoxy-4-methylbenzaldehyde (5) [6] with

† Part 737, T. Kametani, *et al.*, *Heterocycles*, 1977, **7**, 919.

[1] J. S. Webb, D. B. Cosulich, J. H. Mowat, J. B. Patrick, R. W. Broschard, W. E. Meyer, R. P. Williams, C. F. Wolf, W. Fulmor, C. Pidacks, and J. E. Lancaster, *J. Amer. Chem. Soc.*, 1962, **84**, 3185, 3187.

[2] C. L. Stevens, K. G. Taylor, M. E. Munk, W. S. Marshall, K. Noll, G. D. Shah, L. G. Shah, and K. Uzu, *J. Medicin. Chem.*, 1964, **8**, 1.

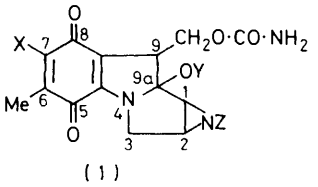
[3] S. Kinoshita, K. Uzu, K. Nakano, M. Shimizu, and T. Takahashi, *J. Medicin. Chem.*, 1971, **14**, 103.

[4] R. W. Franck and J. Auerbach, *J. Org. Chem.*, 1971, **36**, 31.

[5] G. J. Siuta, R. W. Franck, and R. J. Kempton, *J. Org. Chem.*, 1974, **39**, 3739.

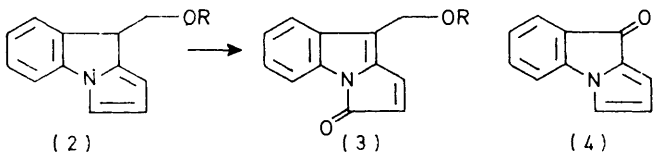
[6] T. Kametani, K. Takahashi, M. Ihara, and K. Fukumoto, *J.C.S. Perkin I*, 1976, 389.

potassium permanganate in aqueous acetone [7] gave the carboxylic acid (6), which after conversion into acid chloride was treated with pyrrolylmagnesium iodide [8,9] in dry ether at room temperature to afford 2-(2-bromo-5-methoxy-4-methylbenzoyl)pyrrole (8). The cyclization was carried out by stirring compound (8) in the presence of sodium hydride and cuprous bromide in dimethylformamide [6] at room temperature for 3 h. The product (10) showed absorptions at 258, 290sh,



(1)

	X	Y	Z
mitomycin A	OMe	Me	H
mitomycin B	OMe	H	Me
mitomycin C	NH_2	Me	H
porfiromycin	NH_2	Me	Me



(2) (3) (4)

SCHEME 1

and 335 nm (log ε 4.18, 3.94, and 3.78) in its u.v. spectrum (in MeOH) and an absorption due to a carbonyl group at 1 690 cm^{-1} in the i.r. spectrum (in $CHCl_3$).

The 6,7-dimethoxy-derivative (11) was also prepared in the similar manner. Thus, 2-bromo-4,5-dimethoxybenzoic acid (7) [10] was converted into the acid chloride, which was condensed with pyrrolylmagnesium iodide. The benzoylpyrrole (9) formed was cyclised with sodium hydride in the presence of cuprous bromide in dimethylformamide.

Photo-oxygenation of 6,7-disubstituted 9-oxo-9*H*-pyrrolo[1,2-*a*]indoles was accomplished as follows. A 200-W tungsten lamp or a 200-W halogen lamp (Ushio) was used as a light source. In this photo-oxygenation, the latter one was more effective. For example, a solution of 9-oxo-7-methoxy-6-methyl-9*H*-pyrrolo[1,2-*a*]-indole (10) in methanol–benzene and in the presence of Rose Bengal under oxygen atmosphere at 25—30 °C was irradiated with a 200-W halogen lamp through a Pyrex filter. After 24 h, the two products formed were isolated by alumina column chromatography followed by silica gel thick-layer chromatography. The structure of the less-polar product, obtained as an unstable solid (32.6% yield), was assigned as the hydroperoxide (14), while that of the more-polar compound, isolated as pale yellowish needles, m.p. 158—159 °C (decomp.) (34.7% yield) was determined as (±)-9,9a-dihydro-3α-hydroxy-9-oxo-7,9aβ-dimethoxy-6-methyl-3*H*-pyrrolo[1,2-*a*]-indole (16). The former compound (14) was converted into the latter (16) by treatment with dimethyl sulphide or further irradiation in methanol. If the above reaction mixture was irradiated for a further 24 h under similar conditions to those described except for a nitrogen atmosphere, only the hydroxy-compound (16) was obtained (71.4% yield). The i.r. spectrum (in $CHCl_3$) of compound (16) showed a carbonyl absorption at 1 708 cm^{-1}, and the u.v. spectrum [$\lambda_{max.}$ (in MeOH) 235, 269sh, and 337 nm (log ε 4.13, 3.74, and 3.18)] suggested a skeleton of 2,2-disubstituted 5-methoxy-3-oxoindole.[11] The n.m.r. spectrum (in $CDCl_3$) gave the signals due to a *C*-methyl group at 2.30 as a singlet, two *O*-methyl groups at 3.35 and 3.80 as singlets, one methine proton at 5.30 as a broad singlet, and two olefinic protons at 6.07 as a broad singlet in addition to two aromatic protons at 6.97 and 7.05 p.p.m. as singlets. A molecular ion peak was observed at *m/e* 261 in the mass spectrum. On acetylation with acetic anhydride in pyridine, the hydroxide (16) afforded the acetate (17), the n.m.r. spectrum (in $CDCl_3$) of which exhibited the methine proton attached to the acetoxy-group at 6.39 p.p.m. as a doublet with *J* 2 Hz. Such a deshielding of the methine proton by acetylation suggests that the hydroxy-group existed at the 3-position and structure (24) of the other possible isomer was eliminated.

The hydroperoxide (14) showed a molecular ion peak at *m/e* 277.0916 ($C_{14}H_{15}NO_5$) in addition to the fragment ion peaks at *m/e* 259 (22) and 260 (23) in the mass spectrum and also gave a positive starch–iodide test.

Irradiation of 6,7-dimethoxy-9-oxo-9*H*-pyrrolo[1,2-*a*]-indole (11) in methanol–benzene in the presence of Rose Bengal under an oxygen atmosphere for 24 h also formed a mixture of the corresponding hydroperoxide (15) and the hydroxide (18). Further irradiation of the resulting mixture under nitrogen for 24 h yielded, as a sole product, the hydroxide (18). The methine proton at the 3-position observed at 5.37 p.p.m. as a broad singlet in the n.m.r. spectrum (in $CDCl_3$) was again shifted to 6.38 p.p.m. as doublet with *J* 2 Hz in case of the acetate (19).

The photo-oxygenation of compound (10) was also carried out in different alcohols in the presence of Rose Bengal. The rate of consumption of the starting material seemed to be the slower, with the higher alcohols. The irradiation of compound (10) in ethanol in a current of oxygen for 36 h followed by the irradiation in a current of nitrogen for 12 h gave the (±)-9aβ-ethoxy-3*H*-pyrrolo[1,2-*a*]indole (20) in 41% yield. On the other hand, the isopropyloxy-compound (21) was obtained (32% yield) by the irradiation of compound (10) in isopropyl alcohol under conditions similar to those described above.

Although dye-sensitized photo-oxygenations of pyrroles have been widely studied, there are few reports describing the mechanism of its initial reaction with

[7] D. H. R. Barton, R. B. Boar, and D. A. Widdowson, *J. Chem. Soc.* (*C*), 1970, 1208.

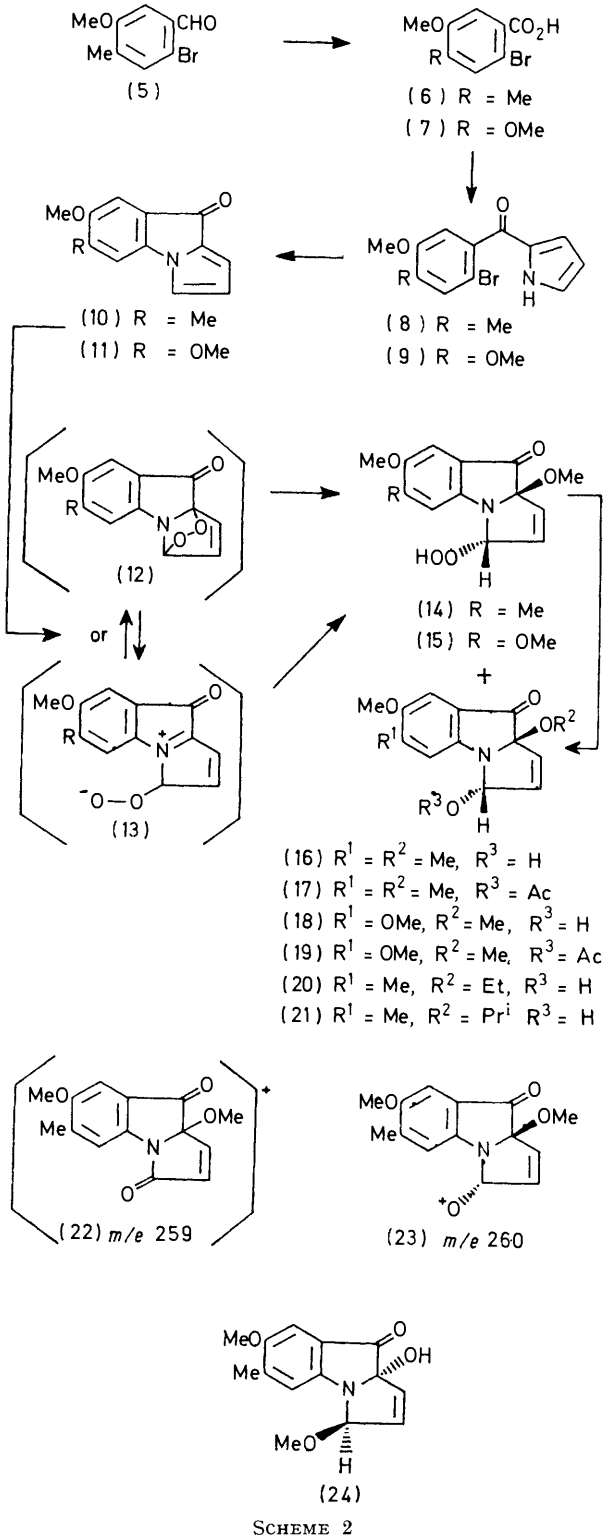
[8] H. Rapoport and C. D. Willson, *J. Amer. Chem. Soc.*, 1962, **84**, 630.

[9] P. S. Skell and G. P. Bean, *J. Amer. Chem. Soc.*, 1962, **84**, 4655.

[10] T. Heap, T. G. H. Jones, and R. Robinson, *J. Chem. Soc.*, 1927, 2021.

[11] A. I. Scott, 'Interpretation of the Ultraviolet Spectra of Natural Products,' Pergamon Press, Oxford, 1964, p. 298.

singlet oxygen.[12,13] It has been assumed that the major final products arise from an *endo*-peroxide intermediate,



SCHEME 2

which is derived from 1,4-cycloaddition of singlet oxygen to the pyrroles. However, it is still doubtful whether the cycloaddition is concerted or involves intermediates. We may account for the formation of the hydroperoxides (14) and (15) *via* the *endo*-peroxide (12) or the zwitterionic intermediate (13). The transformation of the hydroperoxide (14) to the hydroxide (16) would result in photoreduction in alcoholic solution.[14] In view of the regioselective formation of the 9a-methoxy-compound, the zwitterionic intermediate (13), which was directly formed by the reaction of singlet oxygen with the pyrroloindoles, is more likely. Thus the addition of singlet oxygen would first occur at the unsubstituted 3-position. The methoxide ion attacked from the less sterically hindered site and the methoxy-group at C-9a is *trans* to the hydroperoxy- or the hydroxy-group at the 3-position.

The *trans*-configuration of two oxo-substituents at C-3 and C-9a was further supported by the chemical shift due to the methine proton at the 3-position in the n.m.r. spectra, observed at 5.30—5.37 for the hydroxy-compounds (16), (18), (20), and (21) and at 5.57 p.p.m. for the hydroperoxy-compound (14). The BC ring structure should be *cis*. Therefore, if the oxo-substituents at the 3- and 9a-positions are *cis*, the methine proton at the 3-position would exist above the plane of ring A and would be more highly shielded.

EXPERIMENTAL

I.r. and u.v. spectra were taken with Hitachi 215 and Hitachi 124 recording spectrophotometers, respectively. N.m.r. spectra were measured with a JNM-PMX-60 instrument in deuteriochloroform with tetramethylsilane as an internal standard. Mass spectra were measured with Hitachi RMU-7 and JEOL JMS-D100 mass spectrometers.

2-Bromo-5-methoxy-4-methylbenzoic Acid (6).—To a solution of 2-bromo-5-methoxy-4-methylbenzaldehyde (5) (8.2 g) in acetone (100 ml) and water (30 ml) was added potassium permanganate (7.6 g). After the mixture had been stirred for 5 h at room temperature, 10% aqueous potassium hydroxide solution (50 ml) was added. The precipitated manganese dioxide was filtered off and the mother liquor was acidified with 10% hydrochloric acid. The resulting mixture was extracted with chloroform. The extract was washed with water, dried (Na_2SO_4), and evaporated. The resulting crystalline mass was recrystallised from benzene–n-hexane to give the *acid* (6) (4.8 g, 55%) as needles, m.p. 187—188 °C (Found: C, 43.9; H, 3.7. $C_9H_9BrO_3$ requires C, 44.15; H, 3.7%), $\nu_{max.}$($CHCl_3$) 1 695 cm^{-1} (CO_2H); δ($CDCl_3$) 2.23 (3 H, s, 4-Me), 3.87 (3 H, s, 5-OMe), and 7.47 (2 H, s, 3- and 6-H).

2-(2-Bromo-5-methoxy-4-methylbenzoyl)pyrrole (8).—To a solution of the above acid (6) (4 g) in dry benzene (50 ml) was added thionyl chloride (16 g) and the mixture was refluxed for 3 h. After evaporation of the solvent and the excess of the reagent, the resulting crystalline mass was dissolved in dry ether (100 ml). This solution was added dropwise with stirring and cooling to an ethereal solution

[12] D. A. Lightner, *Photochem. Photobiol.*, 1974, **19**, 457.
[13] T. Matsuura and I. Saito, 'Photochemistry of Heterocyclic Compounds,' ed. O. Buchardt, John Wiley and Sons, New York, 1976, pp. 456—523.
[14] A. Schonberg, 'Preparative Organic Photochemistry,' Springer-Verlag, New York, 1968, pp. 193—197.

of pyrrolylmagnesium iodide (50 ml), which was prepared from pyrrole (1.55 g), magnesium turning (450 mg), and ethyl iodide (2.12 g). After the mixture had been stirred for 18 h at room temperature under a nitrogen atmosphere, a saturated aqueous sodium hydrogen carbonate solution was added to it; the whole was then extracted with ether. The extract was washed with brine, a 5% aqueous sodium thiosulphate solution, and brine; it was then dried (Na_2SO_4) and evaporated. The residue was chromatographed on silica gel in benzene–methanol (99 : 1 v/v) to give a powder, which was recrystallised from methanol to afford the 2-*benzoylpyrrole* (8) (2.4 g, 47%) as needles, m.p. 145.5—146 °C (Found: C, 53.25; H, 4.3; N, 4.65. $C_{13}H_{12}NO_2Br$ requires C, 53.1; H, 4.1; N, 4.75%), $\lambda_{max.}$(MeOH) 227 and 302 nm (log ε 3.82 and 3.94); $\nu_{max.}$($CHCl_3$) 3 460 (NH) and 1 620 cm^{-1} (C=O); δ($CDCl_3$) 2.22 (3 H, s, 4-Me), 3.73 (3 H, s, 5-OMe), 6.22 (1 H, m, 4-H), 6.58 (1 H, m, 5-H), 6.87 (1 H, s, 3′-H), 7.10 (1 H, m, 3-H), 7.30 (1 H, s, 6′-H), and 10.3 (1 H, broad s, NH).

7-*Methoxy*-6-*methyl*-9-*oxo*-9H-*pyrrolo*[1,2-a]*indole* (10).—To a solution of the above pyrrole (8) (700 mg) in dry dimethylformamide (20 ml) was added 50% sodium hydride (200 mg). After the mixture had been stirred for 30 min at room temperature, cuprous bromide (170 mg) was added to it and the stirring was continued for 3 h at room temperature under a nitrogen atmosphere. An excess of crystalline ammonium chloride was added to the above mixture which was then evaporated under a reduced pressure. The residue was taken up in chloroform and the extract was washed with water. After drying (Na_2SO_4) the mixture was evaporated to leave a residue, which was chromatographed on silica gel. Benzene eluate afforded a powder, which was recrystallised from benzene to yield the *pyrrolo*[1,2-a]*indole* (10) (270 mg, 53%) as orange prisms, m.p. 178—179 °C (Found: C, 72.95; H, 5.1; N, 6.75. $C_{13}H_{11}NO_2$ requires C, 73.2; H, 5.2; N, 6.55%), $\lambda_{max.}$(MeOH) 335, 290sh, and 258 nm (log ε 3.78, 3.94, and 4.18); $\nu_{max.}$($CHCl_3$) 1 690 cm^{-1} (C=O); δ($CDCl_3$) 2.27 (3 H, s, 6-Me), 3.83 (3 H, s, 7-OMe), 6.17 (1 H, dd, *J* 3 and 4 Hz, 2-H), 6.68 (1 H, d, *J* 4 Hz, 3-H), 6.85 (1 H, s, 5-H), 6.92 (1 H, d, *J* 3 Hz, 1-H), and 7.00 (1 H, s, 8-H); *m/e* 213 (M^+).

2-(2-*Bromo*-4,5-*dimethoxybenzoyl*)*pyrrole* (9).—A mixture of 2-bromo-4,5-dimethoxybenzoic acid (7) [10] (4 g) and thionyl chloride (16 g) in dry benzene (50 ml) was refluxed for 3 h. After evaporation, the resulting crystalline residue was dissolved in a mixture of dry ether (50 ml) and dry tetrahydrofuran (50 ml). The resulting solution was added dropwise with ice cooling to a stirred solution of pyrrolylmagnesium iodide in ether (50 ml) which was prepared from pyrrole (1.5 g), magnesium turning (450 mg), and ethyl iodide (2.1 g). After being stirred for 16 h at room temperature, the reaction mixture was worked up as described above for compound (8) to give the *pyrrolo-derivative* (9) (2 g, 42%) as needles, m.p. 160—161 °C (from methanol) (Found: C, 50.6; H, 3.95; N, 4.3. $C_{13}H_{12}BrNO_3$ requires C, 50.35; H, 3.9; N, 4.5%), $\nu_{max.}$($CHCl_3$) 3 460 (NH) and 1 620 cm^{-1} (C=O); δ($CDCl_3$) 3.83 (3 H, s, O–Me), 3.90 (3 H, s, O–Me), 6.25 (1 H, m, 4-H), 6.62 (1 H, m, 5-H), 7.00 (1 H, s, 3′-H), 7.07 (1 H, s, 6′-H), 7.17 (1 H, m, 5-H), and 10.72 (1 H, broad s, NH).

6,7-*Dimethoxy*-9-*oxo*-9H-*pyrrolo*[1,2-a]*indole* (11).—Cuprous bromide (250 mg) was added to a stirred mixture of the pyrrole (8) (900 mg) and 50% sodium hydride (300 mg) in dry dimethylformamide (20 ml); stirring was continued for 3 h at room temperature under a nitrogen atmosphere. The reaction mixture was worked up as described above for compound (10) to give the *pyrrolo*[1,2-a]*indole* (11) (350 mg, 52%) as orange prisms, m.p. 160—161 °C (from benzene) (Found: C, 68.35; H, 4.8; N, 6.1. $C_{13}H_{11}NO_3$ requires C, 68.1; H, 4.85; N, 6.1%), $\nu_{max.}$($CHCl_3$) 1 690 cm^{-1} (C=O); δ($CDCl_3$) 3.83 (3 H, s, OMe), 3.93 (3 H, s, OMe), 6.16 (1 H, dd, *J* 3 and 4 Hz, 2-H), 6.62 (1 H, s, 5-H), 6.65 (1 H, d, *J* 4 Hz, 3-H), 6.90 (1 H, d, *J* 3 H, 1-H); and 7.06 (1 H, s, 8-H).

Photo-oxygenation of 7-*Methoxy*-6-*methyl*-9-*oxo*-9H-*pyrrolo*[1,2-a]*indole* (10) *in Methanol*.—(*a*) A mixture of compound (10) (200 mg) and Rose Bengal (50 mg) in benzene (50 ml) and methanol (500 ml) was irradiated for 24 h at 25—30 °C in a current of oxygen with a 200-W halogen lamp through a Pyrex filter. After evaporation of the solvents below 40 °C, the residue was partitioned between chloroform and saturated aqueous sodium hydrogen carbonate. The chloroform layer was separated, washed with water, dried (Na_2SO_4), and evaporated. The residue was subjected to chromatography on alumina (grade III) in ether to give a gum, which was further purified by preparative t.l.c. on silica gel, benzene–ether (2 : 1 v/v) being used for development. The upper yellow zone (R_F 0.5) was eluted with chloroform–methanol (9 : 1 v/v) to give (±)-9,9a-*dihydro*-3α-*hydroperoxy*-7,9aβ-*dimethoxy*-6-*methyl*-9-*oxo*-3H-*pyrrolo*[1,2-a]*indole* (14) (85 mg, 32.6%) as a yellow gum (Found: M^+, 277.0916. $C_{14}H_{15}NO_5$ requires M^+, 277.0949), $\nu_{max.}$($CHCl_3$) 1 708 cm^{-1} (C=O); δ($CDCl_3$) 2.32 (3 H, s, 6-Me), 3.36 (3 H, s, 9a-OMe), 3.82 (3 H, s, 7-OMe), 5.57 (1 H, d, *J* 2 Hz, 3-H), 5.97 (1 H, dd, *J* 2 and 5 Hz, 2-H), 6.22 (1 H, d, *J* 5 Hz, 1-H), 7.00 (1 H, s, 5-H), and 7.15 (1 H, s, 8-H); *m/e* 277 (M^+), 260 (M^+ − OH), and 259 (M^+ − H_2O).

The lower yellow zone (R_F 0.25) was eluted with chloroform–methanol (9 : 1 v/v) to give a pale yellow powder, which was recrystallised from benzene to afford (±)-9,9a-*dihydro*-3α-*hydroxy*-7,9aβ-*dimethoxy*-6-*methyl*-9-*oxo*-3H-*pyrrolo*[1,2-a]*indole* (16) (85 mg, 34.7%) as pale yellow needles, m.p. 158—159 °C (decomp.) (Found: C, 64.6; H, 5.65; N, 5.25. $C_{14}H_{15}NO_4$ requires C, 64.35; H, 5.8; N, 5.35%), $\lambda_{max.}$(MeOH) 337, 269sh, and 235 nm (log ε 3.18, 3.74, and 4.13); $\nu_{max.}$($CHCl_3$) 1 708 cm^{-1} (C=O); δ($CDCl_3$) 2.30 (3 H, s, 6-Me), 3.35 (3 H, s, 9a-OMe), 3.80 (3 H, s, 7-OMe), 5.30 (1 H, broad s, 3-H), 6.07 (2 H, broad s, 1 and 2-H), 6.97 (1 H, s, 5-H), and 7.05 (1 H, s, 8-H); *m/e* 261 (M^+).

(*b*) A mixture of compound (10) (200 mg) and Rose Bengal (50 mg) in benzene (50 ml) and methanol (500 ml) was irradiated for 24 h under the same conditions as those described above and then irradiated for 24 h at 25—30 °C in a current of nitrogen with a 200-W halogen lamp through a Pyrex filter. After evaporation of the solvents below 40 °C, the residue was partitioned between chloroform and saturated aqueous sodium hydrogen carbonate. The chloroform layer was washed with water, dried (Na_2SO_4), and evaporated to give a yellowish residue, which was subjected to chromatography on alumina (grade III). Elution with ether followed by evaporation gave a pale yellow powder, which was recrystallised from benzene to afford compound (16) (175 mg, 71.4%) as *pale yellow needles*, m.p. 158—159 °C (decomp.), identical with the sample prepared by method (*a*).

(±)-3α-*Acetoxy*-9,9a-*dihydro*-7,9aβ-*dimethoxy*-6-*methyl*-9-*oxo*-3H-*pyrrolo*[1,2-a]*indole* (17).—A mixture of the above hydroxy-compound (16) (20 mg), pyridine (2 ml), and acetic anhydride (2 ml) was stirred for 15 h at room temperature.

The resulting mixture was poured into ice–water–saturated aqueous potassium hydrogen sulphate mixture and then extracted with chloroform. The combined chloroform layers were washed with a saturated aqueous potassium hydrogen sulphate, water, saturated aqueous sodium hydrogen carbonate, and water. After drying (Na_2SO_4), the mixture was evaporated to give a yellow gum, which was subjected to a preparative t.l.c. on silica gel, benzene–ether (2 : 1 v/v) being used for development. The yellowish zone (R_F 0.8) was eluted with chloroform–methanol (9 : 1 v/v) to give the acetate (17) (16 mg, 72%) as yellowish gum (Found: M^+, 303.1084. $C_{16}H_{17}NO_5$ requires M^+, 303.1106), $\nu_{max.}$($CHCl_3$) 1 735 and 1 705 cm^{-1} (C=O); δ($CDCl_3$) 2.22 (3 H, s, 3-Ac), 2.30 (3 H, s, 6-Me), 3.40 (3 H, s, 9a-OMe), 3.88 (3 H, s, 7-OMe), 6.06 (1 H, dd, *J* 2 and 5 Hz, 2-H), 6.20 (1 H, d, *J* 5 Hz, 1-H), 6.39 (1 H, d, *J* 2 Hz, 3-H), 7.00 (1 H, s, 5-H), and 7.48 (1 H, s, 8-H); *m/e* 303 (M^+).

(±)-9,9a-*Dihydro*-3α-*hydroxy*-6,7,9aβ-*trimethoxy*-9-*oxo*-3H-*pyrrolo*[1,2-a]*indole* (18).—A mixture of compound (11) (200 mg) and Rose Bengal (50 mg) in benzene (50 ml) and methanol (500 ml) was irradiated with a 200-W halogen lamp through Pyrex filter at 25—30 °C in a current of oxygen for 24 h and then a current of nitrogen for 24 h. After evaporation of the solvent below 40 °C, the residue was partitioned between chloroform and saturated aqueous sodium hydrogen carbonate. The chloroform layer was separated, washed with water, dried (Na_2SO_4), and evaporated to give a yellow gum, which was subjected to chromatography on alumina (grade III). Evaporation of an ethereal eluate gave a residue, which was further purified by preparative t.l.c. on silica gel benzene–methanol (9 : 1 v/v) being twice used for development. The yellowish zone (R_F 0.3) was eluted with chloroform–methanol (9 : 1 v/v) to yield compound (18) (45 mg, 19%) as a yellow syrup, which failed to crystallise (Found: M^+, 277.0944. $C_{14}H_{15}NO_5$ requires M^+, 277.0950), $\nu_{max.}$($CHCl_3$) 1 705 cm^{-1} (C=O); δ 3.33 (3 H, s, 9a-OMe), 3.82 (3 H, s, OMe), 3.95 (3 H, s, OMe), 5.37 (1 H, broad s, 3-H), 6.03 (2 H, s, 1- and 2-H), 6.73 (1 H, s, 5-H), and 6.98 (1 H, s, 8-H); *m/e* 277 (M^+).

(±)-3α-*Acetoxy*-9,9a-*dihydro*-6,7,9aβ-*trimethoxy*-9-*oxo*-3H-*pyrrolo*[1,2-a]*indole* (19).—A mixture of the above compound (18) (30 mg) and acetic anhydride (2 ml) in pyridine (2 ml) was stirred for 15 h at room temperature and the resulting mixture was worked up as in the case of the acetate (17). Purification of the product by preparative t.l.c. on silica gel, benzene–methanol (9 : 1 v/v) being twice used for development, gave compound (19) (25 mg, 79%) as a yellow gum, which was too unstable for crystallisation (Found: M^+, 319.1051. $C_{16}H_{17}NO_6$ requires M^+, 319.1055), $\nu_{max.}$($CHCl_3$) 1 735 and 1 705 cm^{-1} (C=O); δ($CDCl_3$) 2.22 (3 H, s, Ac), 3.36 (3 H, s, 9a-OMe), 3.87 (3 H, s, OMe), 4.03 (3 H, s, OMe), 6.07 (1 H, dd, *J* 2 and 5 Hz, 2-H), 6.25 (1 H, d, *J* 5 Hz, 1-H), 6.38 (1 H, d, *J* 2 Hz, 3-H), 7.00 (1 H, s, 5-H), and 7.32 (1 H, s, 8-H); *m/e* 319 (M^+).

(±)-9,9a-*Dihydro*-9aβ-*ethoxy*-3α-*hydroxy*-7-*methoxy*-6-*methyl*-9-*oxo*-3H-*pyrrolo*[1,2-a]*indole* (20).—A mixture of compound (10) (200 mg) and Rose Bengal (50 mg) in benzene (50 ml) and ethanol (500 ml) was irradiated *via* a Pyrex filter with a 200-W halogen lamp, first in a current of oxygen for 36 h and then in a current of nitrogen for 12 h at 25—30 °C. After evaporation of the solvent below 40 °C, the residue was partitioned between chloroform and saturated aqueous sodium hydrogen carbonate. The chloroform layer was separated, washed with water, dried (Na_2SO_4), and evaporated to give a yellow gum, whose ethereal solution was subjected to chromatography on alumina (grade III). Recrystallisation of the resulting yellow powder from benzene–n-hexane afforded compound (20) (103 mg, 41%) as pale yellow *needles*, m.p. 133—134 °C (decomp.) (Found: C, 65.5; H, 6.0; N, 4.85. $C_{15}H_{17}NO_4$ requires C, 65.45; H, 6.2; N, 5.1%), $\nu_{max.}$($CHCl_3$) 1 705 cm^{-1} (C=O); δ($CDCl_3$) 1.23 (3 H, t, *J* 7 Hz, OCH_2CH_3), 2.32 (3 H, s, 6-Me), 3.65 (2 H, q, *J* 7 Hz, OCH_2CH_3), 3.80 (3 H, s, 7-OMe), 5.33 (1 H, broad s, 3-H), 6.08 (2 H, s, 1- and 2-H), 6.98 (1 H, s, 5-H), and 7.07 (1 H, s, 8-H); *m/e* 275 (M^+).

(±)-9,9a-*Dihydro*-3α-*hydroxy*-9aβ-*isopropyloxy*-7-*methoxy*-6-*methyl*-9-*oxo*-3H-*pyrrolo*[1,2-a]*indole* (21).—A mixture of compound (10) (250 mg) and Rose Bengal (200 mg) in isopropyl alcohol (500 ml) and benzene (50 ml) was irradiated and then worked up as above. Recrystallisation of the resulting yellow powder from benzene–n-hexane afforded compound (21) (112 mg, 32%) as *pale yellow needles*, m.p. 148—150 °C (decomp.) (Found: C, 65.15; H, 6.2; N, 4.7. $C_{16}H_{19}NO_4 \cdot 0.25H_2O$ requires C, 65.4; H, 6.7; N, 4.75%), $\nu_{max.}$($CHCl_3$) 1 708 cm^{-1} (C=O); δ($CDCl_3$) 1.15 [3 H, d, *J* 6 Hz, $CH(CH_3)CH_3$], 1.22 [3 H, d, *J* 6 Hz, $CH(CH_3)CH_3$], 2.32 (3 H, s, 6-Me), 3.78 (3 H, s, 7-OMe), 5.30 (1 H, broad s, 3-H), 6.00 (2 H, s, 1- and 2-H), 6.93 (1 H, s, 5-H), and 7.03 (1 H, s, 8-H); *m/e* 289 (M^+).

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