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CONVERSION OF INDOLES INTO QUINOLINES THROUGH THE N-1–C-2 FISSION BY SINGLET-OXYGEN AS A MODEL EXPERIMENT OF BIOMIMETIC SYNTHESIS OF QUININE ALKALOIDS

MASATAKA IHARA, KAZUHARU NOGUCHI and KEIICHIRO FUKUMOTO*
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan

and

TETSUJI KAMETANI*
Institute of Medicinal Chemistry, Hoshi University, Ebara 2-4-41, Sinagawa-ku, Tokyo 142, Japan

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Abstract—Photo-oxygenation of indole-3-acetaldehydes (**28–30**) followed by treatments with dimethyl sulphide and then dilute acetic acid gave 4-acylquinolines (**13**, **31** and **32**), respectively.

It is now well known that several alkaloids are biosynthesized through reconstruction from indole alkaloids. For example, streptonigrin (**1**) is derived via fission of the N-1–C-7a bond[1] (a) of indole while the cleavage at the N-1–C-2 bond (b) leads to quinine (**2**)[2] and the C-2–C-3 bond fission (c) to camptothecin (**3**).[3] Suggestion of the important role of molecular oxygen for the cleavage of indoles stimulated extensive studies of reaction of indoles, including tryptophan, with molecular oxygen. As a result of the efforts, the conversion of indoles into quinolines through the C-2–C-3 bond fission (c) has been accomplished using singlet oxygen.[4–6] Utilizing this type of reaction we have, recently, synthesized (±)-camptothecin (**3**) by two different routes[7,8] via the photo-oxygenation of indoles, such as **4**, followed by the basic treatment of the resulting keto-amide (**5**) to quinoline (**6**). The quinoline derivative (**6**) was transformed into (±)-camptothecin (**3**) by Winterfeldt's method.[9]

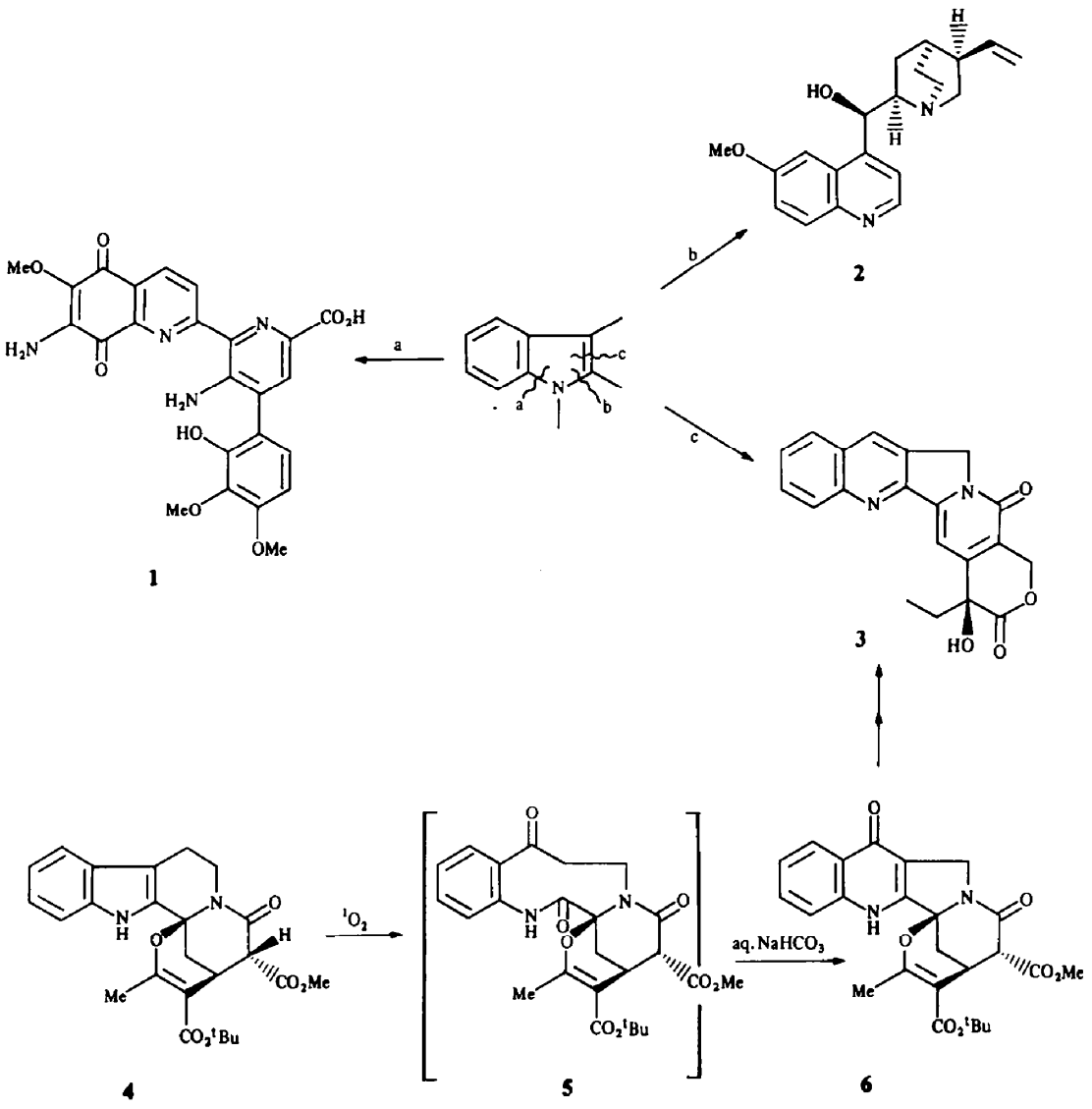
It has been demonstrated by tracer experiments, using *Cinchona ledgeriana*, that corynantheal (**7**) is a precursor in the biosynthesis of quinine alkaloids.[2] Furthermore, several intermediates, cinchonaminal (**8**) → the imine (**9**) → the 9-ketoquinoline base (**10**), were postulated for the transformation.[2] To mimic the biogenesis, van Tamelen and Haarstad[10] converted 2-methyltryptophan (**11**) into 4-acetylquinoline (**13**) in 20% yield using sodium hypochlorite. However, this oxidation procedure has not been further applied to the synthesis of quinine alkaloids mainly due to its drastic conditions. To the best of our knowledge, the formation of quinolines from indoles through N-1–C-2 fission (b) utilizing singlet oxygen, which seems to take place under mild conditions, has not been reported. To test the hypothesis of the biogenesis of quinine and to develop new synthetic route for this pharmacologically important alkaloid, we examined the photo-oxygenation of indole-3-acetic acids and indole-3-acetaldehydes and we report here our success.†

Firstly, we examined the photo-oxygenation of N-benzylindole-3-acetic acid (**14**)[12] and N-benzyl-2-methylindole-3-acetic acid (**15**), which were prepared in high yield by selective N-benzylation of their corresponding N-nor derivatives[13] using 1.2 equivalents of benzyl bromide and 2.4 equivalents of sodium hydride in dimethylformamide. When **14** was irradiated at 0° for 3 hr with a 200 W halogen lamp in the presence of Rose Bengal in methanol in a flow of oxygen, the formation of a single product, assumed to be the tricyclic hydroperoxide (**16**), was observed on TLC analysis. The product was then treated, without isolation, with dimethyl sulphide for 2 hr to give, from **14**, the hydroxylactone (**18**) in 96.2% yield after purification by silica gel column chromatography. In a similar way, **15** was converted into the corresponding lactone (**19**) in quantitative yield.

These tricyclic lactones (**18** and **19**) were treated under both acidic and basic conditions in order to synthesize the 2-quinolone derivatives (**24** and **25**), but the following unexpected products were obtained. Reaction of **18** with a mixture of 10% hydrochloric acid–methanol (1 : 1) at room temperature for 10 hr gave the ester (**20**), in 68.3% yield, whose UV spectrum [(MeOH) λ_{max} nm (ε) 249 (9338) and 286 (2886)] indicated the 2-oxindole structure.[14] This compound should be formed by methanolysis of **18** and dehydration. On the other hand, the same treatment of **19** for 12 hr afforded the methyl ester (**22**) in 71.3% yield, which should be produced by methanolysis, dehydration to the olefin (**21**) and a successive S_N2' type reaction. Reaction of **19** with 10% methanolic potassium hydroxide at room temperature for 12 hr produced hydrolysis of the lactone and tandem rearrangement[15] giving the carboxylic acid (**23**) in 96.7% yield. Its UV spectrum [(MeOH) λ_{max} nm (ε) 233 (24,443), 258 (6495) and 400 (3090)] clearly suggested the 3-oxindole structure (**23**).[14]

Next, photo-oxygenation of N-benzyl-2-methylindole-3-acetaldehyde (**26**), prepared in 90.8% yield from the acid (**15**) on esterification followed by reduction with di-isobutylaluminum hydride, was tested. The lactol (**27**) was obtained as a 1 : 1 mixture of two epimers in 81.5% yield by the dye-induced photo-oxidation of **26** followed by reduction with dimethyl sulphide. Acidic treatments of **27** gave an intractable polar product, expected to be a quaternary base.

† A part of this work has been reported as a preliminary communication.[11]



Scheme 1.

Finally, the requisite transformation of indoles to quinolines was achieved starting from the N-unsubstituted aldehydes (**28–30**).

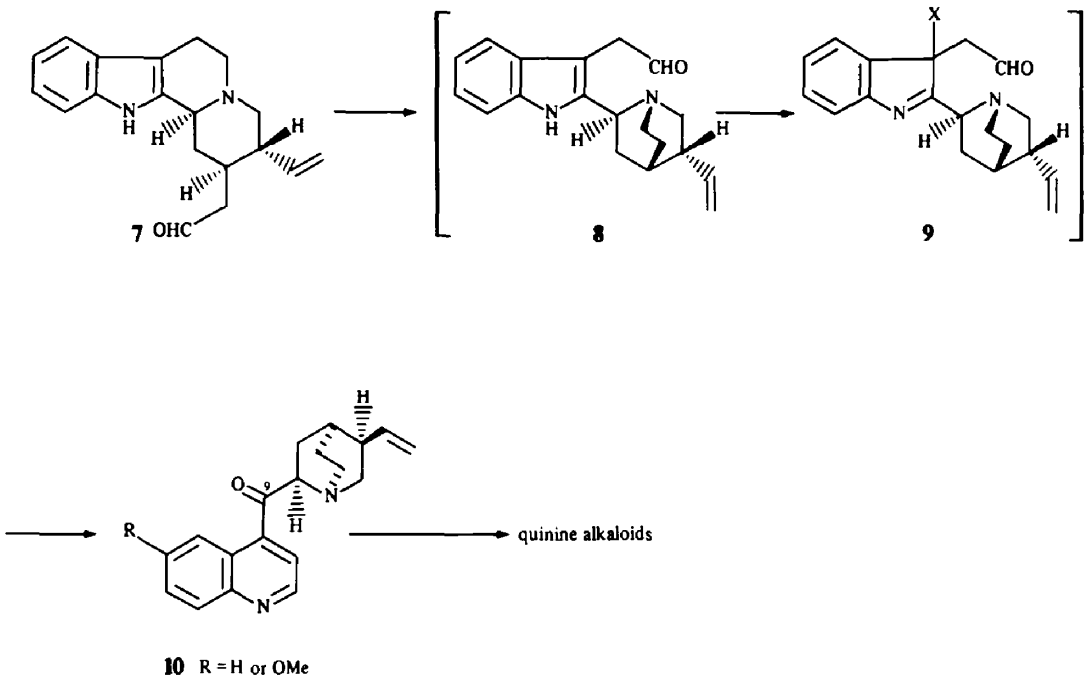
Indole-3-acetaldehyde (**28**)[16] and its 2-methyl derivative (**29**)[17] were prepared by reduction of the corresponding methyl ester with di-isobutylaluminum hydride at −78°, whereas 2-phenylindole-3-acetaldehyde (**30**) was synthesized by reaction of the corresponding nitrile with the same reducing agent at −78°. The aldehydes (**28–30**) were subjected to photo-oxygenation for 3 hr at 0° followed by treatment with dimethyl sulphide for 2 hr at ambient temperature. After evaporation of both solvent and reagents, the crude products were, respectively, reacted with a mixture of acetic acid–tetrahydrofuran–water (3:2:2) at ambient temperature for 10 hr. The desired quinolines (**13**,[20] **31**[19] and **32**[20]) were obtained in 16.3%, 62.6% and 75.7% yield, respectively, and their structure determined by comparison with authentic samples.

The synthesis of quinine alkaloids using the above procedure is in progress.

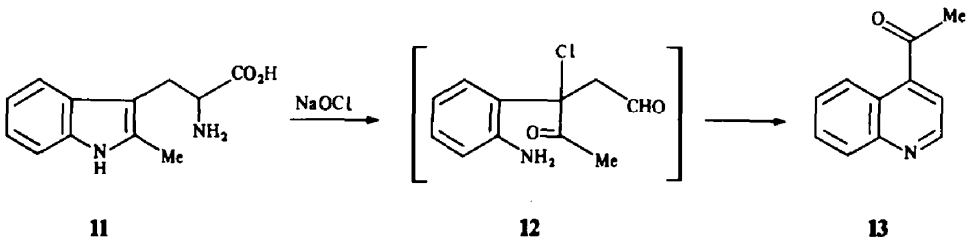
EXPERIMENTAL

UV spectra were measured with a Hitachi 124 spectrometer, IR spectra with a Hitachi 260-10 spectrometer and NMR spectra with JEOL-PMX-60 and JEOL-PS-100 spectrometers. Ordinary mass spectra were obtained with a Hitachi M-52G while accurate mass spectra were taken with a JEOL-JMS-01SG-2 spectrometer.

N-Benzylindole-3-acetic acid (**14**). To a soln of indole-3-acetic acid (1 g, 5.71 mmol) in dry DMF (10 ml) was added 60% NaH (0.55 g, 13.8 mmol) under ice cooling and the mixture was stirred for 30 min at 0°. After addition of benzyl bromide (1.17 g, 6.84 mmol), the resulting mixture was stirred for 1 hr at 0° and then poured into H_2O (100 ml). Acidification of the mixture with 10% HCl followed by standing for 12 hr in a refrigerator gave a solid which was recrystallized from petrol ether to afford **14** (1.48 g, 97.7%) as colourless needles, m.p. 152–153° (lit.[12] m.p. 148°); IR $\nu_{max}^{CHCl_3}$ 1700 cm^{-1} (CO);



Biosynthesis of quinine alkaloids.



Scheme 2.

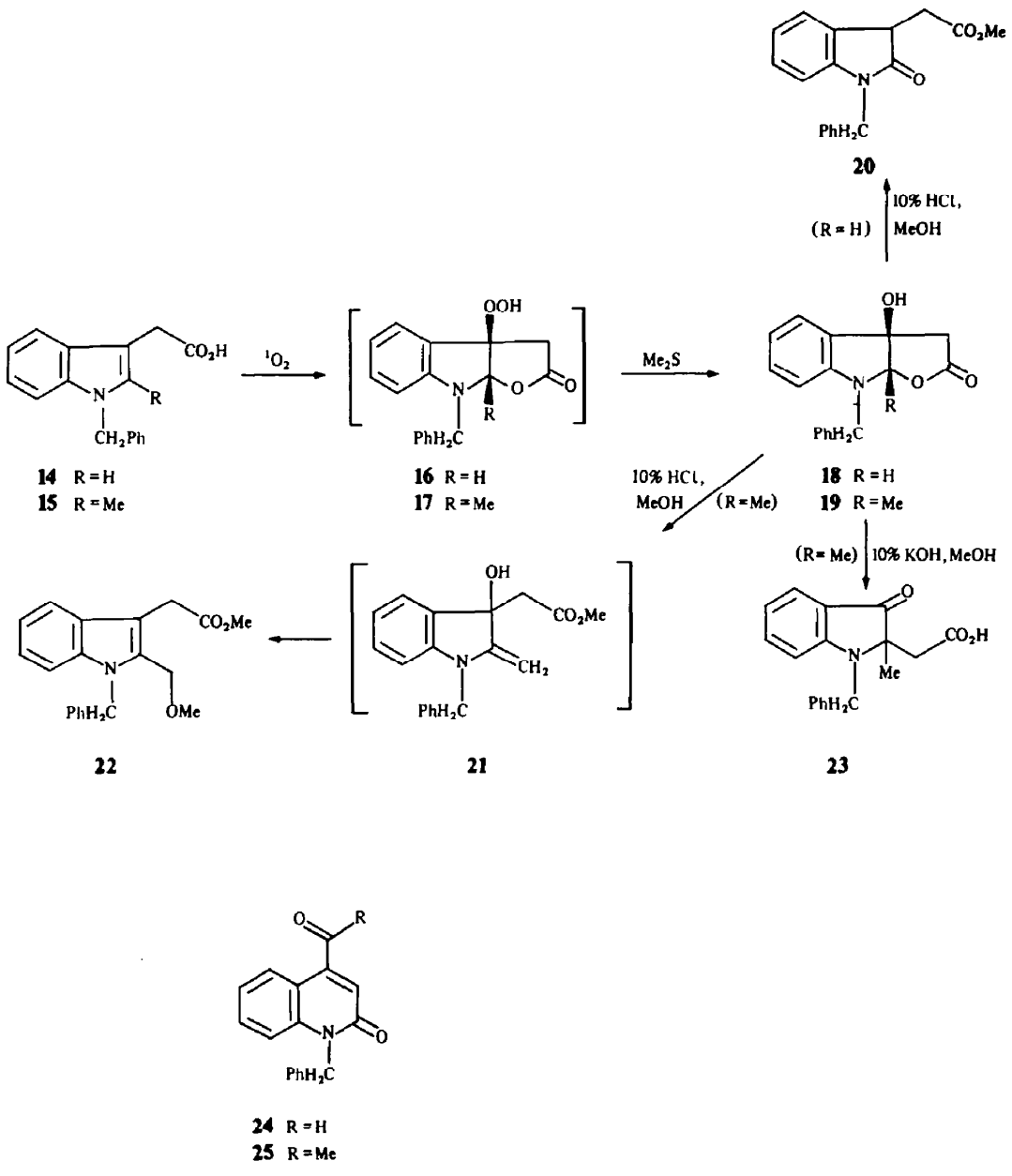
^{1}H-NMR ($CDCl_3$) δ 3.70 (2H, s, $C\underline{H}_2CO_2H$), 5.10 (2H, s, $NC\underline{H}_2Ph$), 6.67–7.63 (10H, m, 10 × ArH), 9.20 (1H, br s, CO_2H); MS *m/z* 265 $[M]^+$.

N-*Benzyl*-2-*methylindole*-3-*acetic acid* (**15**). Reaction of 2-methylindole-3-acetic acid[13] (1 g, 5.29 mmol), 60% NaH (0.51 g, 12.8 mmol) and benzyl bromide (1.09 g, 6.37 mmol) in dry DMF (10 ml) was carried out and worked-up as above to give **15** (1.13 g, 76.6%) as colourless pillars, m.p. 178–179° (from petrol ether); IR $\nu_{max}^{CHCl_3}$ 1700 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ 2.30 (3H, s, Me-2), 3.70 (2H, s, $C\underline{H}_2CO_2H$), 5.21 (2H, s, $NC\underline{H}_2Ph$), 6.60–7.67 (9H, m, 9 × ArH), 8.56 (1H, br s, CO_2H); MS *m/z* 279 $[M]^+$. (Found: C, 76.91; H, 6.01; N, 4.86%. Calc for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; N, 5.01%.)

N-*Benzyl*-2,3,3a,8aβ-*tetrahydro*-3aβ-hydroxyfuro(2,3-b)*indol*-2-*one* (**18**). A soln of **14** (200 mg, 0.755 mmol) and Rose Bengal (30 mg) in MeOH (20 ml) was irradiated with a 200 W halogen lamp through a Pyrex filter for 3 hr in a flow of O_2 at 0°. After addition of Me_2S (0.5 ml), the mixture was stirred for 2 hr at room temp and then evaporated. The residue was partitioned between sat $NaHCO_3$ aq and $CHCl_3$. The organic layer was washed with H_2O, dried over Na_2SO_4 and evaporated to give a residue which was subjected to silica gel column chromatography. Elution with $CHCl_3$ afforded **18** (204 mg, 96.2%) as a pale yellow syrup; IR $\nu_{max}^{CHCl_3}$ 3550 (OH), 1770 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ 3.03 (2H, s, 3-H_2), 4.47 (2H, s, $NC\underline{H}_2Ph$), 5.53 (1H, s, H-8a), 6.33–7.77 (9H, m, 9 × ArH); MS *m/z* 281 $[M]^+$; exact mass calc for $C_{17}H_{15}NO_3$ 281.1050, found 281.1035.

N-*Benzyl*-2,3,3a,8a-*tetrahydro*-3aβ-*hydroxy*-8aβ-*methylfuro*(2,3-b)*indol*-2-*one* (**19**). Photo-oxygenation of **15** (200 mg, 0.717 mmol) followed by work-up and purification as above gave a solid, which was recrystallized from C_6H_6–n-hexane to afford **19** (211 mg, 100%) as colourless needles, m.p. 157–158°; IR $\nu_{max}^{CHCl_3}$ 3570 (OH), 1760 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ 1.63 (3H, s, Me-8a), 2.96 (2H, s, 3-H_2), 4.23 and 4.63 (each 1H, each d, J = 17 Hz, $NC\underline{H}_2Ph$); MS *m/z* 295 $[M]^+$. (Found: C, 72.83; H, 5.87; N, 4.61%. Calc for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74%.)

N-*Benzyl*-2,3-*dihydro*-3-(*methoxycarbonylmethyl*)*indol*-2-*one* (**20**). A soln of **18** (53 mg, 0.189 mmol) and 10% HCl (1 ml) in MeOH (1 ml) was stirred for 10 hr at room temp. After neutralization using sat $NaHCO_3$ aq, the mixture was



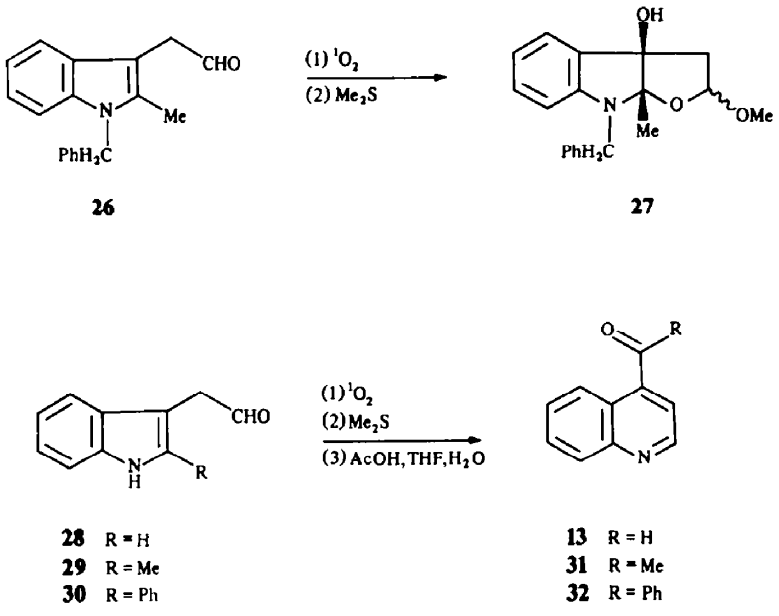
24 R = H
25 R = Me

Scheme 3.

extracted with $CHCl_3$. The extract was washed with H_2O, dried over Na_2SO_4 and evaporated to give a residue, which was purified by column chromatography on silica gel. Elution with C_6H_6–Me_2CO (49:1) afforded **20** (38 mg, 68.3%) as a pale yellow syrup; UV λ_{max}^{MeOH} 249 (9338), 286 nm (2886); IR $\nu_{max}^{CHCl_3}$ 1725, 1700 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ 2.77 (1H, dd, J = 8 and 17 Hz, —C<u>H</u>HCO$_2$Me), 3.17 (1H, dd, J = 5 and 17 Hz, —CH<u>H</u>CO$_2$Me), 3.61 (3H, s, OMe), 3.84 (1H, dd, J = 5 and 8 Hz, H-3), 4.87 (2H, s, NC<u>H</u>$_2$Ph), 6.56–7.60 (9H, m, 9 × ArH); MS *m/z* 295 $[M]^+$. (Found: C, 72.91; H, 5.68; N, 4.58%. Calc for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74%.)

N - *Benzyl* - 2 - (2 - *methoxymethyl*) - 3 - (*methoxycarbonylmethyl*)*indole* (**22**). A soln of **19** (133 mg, 0.451 mmol) and 10% HCl (3 ml) in MeOH (3 ml) was stirred for 12 hr at room temp and then neutralized with sat $NaHCO_3$ aq. Extraction with $CHCl_3$, followed by washing the extract with H_2O, drying over Na_2SO_4 and evaporation gave a residue which was chromatographed on silica gel. Elution with C_6H_6 yielded **22** (100 mg, 71.3%) as a brownish syrup; IR $\nu_{max}^{CHCl_3}$ 1720 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ 3.23 (3H, s, OMe), 3.60 (3H, s, CO_2Me), 3.77 (2H, s, C<u>H</u>$_2$CO$_2$Me), 4.50 (2H, s, C<u>H</u>$_2$OMe), 5.36 (2H, s, NC<u>H</u>$_2$Ph), 6.80–7.80 (9H, m, 9 × ArH); MS *m/z* 323 $[M]^+$. (Found: C, 72.92; H, 6.15; N, 4.33%. Calc for $C_{20}H_{21}NO_3 \cdot 0.25\,H_2O$: C, 73.26; H, 6.56; N, 4.27%.)

N - *Benzyl* - 2 - (*carboxymethyl*) - 2,3 - *dihydro* - 2 - *methylindol* - 3 - *one* (**23**). A soln of **19** (180 mg, 0.610 mmol) in 10% (w/v) KOH–MeOH (5 ml) was stirred for 12 hr at room temp. After acidification with 10% HCl, the mixture was extracted with $CHCl_3$. The extract was washed with brine, dried over Na_2SO_4 and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with $CHCl_3$–MeOH (99:1) afforded **23** (174 mg, 96.7%) as a pale yellow syrup; UV λ_{max}^{MeOH} 233 (24,443), 258 (6495), 400 nm (3090); IR $\nu_{max}^{CHCl_3}$ 1710, 1690 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ 1.26 (3H, s, Me-2), 2.57 and 2.97 (each 1H, each d, J = 16 Hz, C<u>H</u>$_2$CO$_2$H), 4.50 (2H, s, NC<u>H</u>$_2$Ph), 6.40–



Scheme 4.

7.70 (9H, m, 9 × ArH), 8.30 (1H, br s, CO_2H); MS *m/z* 295 $[M]^+$. (Found: C, 72.97; H, 5.39; N, 4.42%. Calc for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74%.)

N - *Benzyl* - 2 - *methylindole* - 3 - *acetaldehyde* (**26**). A soln of **15** (1 g, 3.58 mmol) in 5% (w/v) H_2SO_4–MeOH (20 ml) was stirred for 1 hr at room temp and then poured into sat $NaHCO_3$ aq under cooling with ice. The mixture was extracted with $CHCl_3$ and the extract was washed with H_2O and dried over Na_2SO_4. Evaporation of the solvent gave a residue which was purified by silica gel column chromatography. Elution with $CHCl_3$ yielded the corresponding ester (1.05 g, 100%).

To a soln of the above ester (1 g, 3.41 mmol) in a mixture of dry CH_2Cl_2 (20 ml) and dry DME (20 ml) was added 25% (w/v) DIBAL–toluene (2.91 ml) at −78° under stirring and the mixture continued to be stirred for 1 hr at −78° before being poured into 10% HCl. After extraction with C_6H_6 the extract was washed with H_2O, dried over Na_2SO_4 and evaporated. The residue was chromatographed on silica gel, eluting with benzene, to afford **26** (0.806 g, 90.8%) as a colourless syrup; IR $\nu_{max}^{CHCl_3}$ 1720 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ 2.30 (3H, s, Me-2), 3.72 (2H, d, J = 2.4 Hz, C<u>H</u>$_2$CHO), 5.28 (2H, s, NC<u>H</u>$_2$Ph), 6.70–7.60 (9H, m, 9 × ArH), 9.60 (1H, d, J = 2.4 Hz, CHO); MS *m/z* 263 $[M]^+$. (Found: C, 81.71; H, 6.50; N, 5.37%. Calc for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32%.)

Indole-3-acetaldehyde (**28**). Indole-3-acetic acid (1 g, 5.71 mmol) was converted into the methyl ester (1.02 g, 94.4%) as above. Reduction of the methyl ester (1.17 g, 6.19 mmol) with 25% (w/v) DIBAL–toluene in a mixture of dry CH_2Cl_2 (20 ml) and dry DME (20 ml) followed by work-up, as above, gave a residue which was purified by silica gel chromatography. Elution with $CHCl_3$ afforded **28**[16] (0.738 g, 75%) as a colourless syrup; IR $\nu_{max}^{CHCl_3}$ 3470 (NH), 1720 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ 3.97 (2H, d, J = 2.6 Hz, C<u>H</u>$_2$CHO), 6.77–7.50 (5H, m, 5 × ArH), 8.17 (1H, br s, NH), 9.53 (1H, t, J = 2.6 Hz, CHO); MS *m/z* 159 $[M]^+$; exact mass calc for $C_{10}H_9NO$ 159.0684, found 159.0686.

2 - *Methylindole* - 3 - *acetaldehyde* (**29**). Methyl 2 - methylindole-3-acetate (0.65 g, 3.2 mmol), prepared from the corresponding acid, was reduced using 25% (w/v) DIBAL–toluene (2.73 ml) in a mixture of dry CH_2Cl_2 (15 ml) and dry DME (15 ml) and then worked-up, as above, to afford **29**[17] (465 mg, 83.9%) as a pale yellow syrup; IR $\nu_{max}^{CHCl_3}$ 3460 (NH), 1720 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ 2.30 (3H, s, Me-2), 3.63 (2H, d, J = 2.8 Hz, C<u>H</u>$_2$CHO), 6.80–7.50 (4H, m, 4 × ArH), 7.90 (1H, br s, NH), 9.56 (1H, t, J = 2.8 Hz, CHO); MS *m/z* 173 $[M]^+$; exact mass calc for $C_{11}H_{11}NO$ 173.0841, found 173.0866.

2-*Phenylindole-3-acetaldehyde* (**30**). To a soln of 2-phenylindole-3-acetonitrile[18] (484 mg, 2.09 mmol) in dry toluene (20 ml) was added 25% (w/v) DIBAL–n-hexane (1.43 ml) at −78° under stirring and the mixture then continued to be stirred for 30 min at −78°. After addition of H_2O (0.4 ml) and C_6H_6 (30 ml), the resulting mixture was further stirred for 3 hr at room temp and then filtered through Celite. Evaporation of the mother liquor gave a residue, which was subjected to column chromatography on silica gel. Elution with $CHCl_3$ yielded **30** (120 mg, 24.4%) as a brownish syrup; IR $\nu_{max}^{CHCl_3}$ 3480 (NH), 1725 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ 3.73 (2H, d, J = 2.5 Hz, C<u>H</u>$_2$CHO), 6.40–8.30 (10H, m, 10 × ArH), 9.54 (1H, t, J = 2.5 Hz, CHO); MS *m/z* 235 $[M]^+$; exact mass calc for $C_{16}H_{13}NO$ 235.0998, found 235.1016.

(±) - N - *Benzyl* - 2,3,3a,8a - *tetrahydro* - 3a*β* - *hydroxy* - 2 - *methoxy* - 8a*β* - *methylfuro*(2,3 - b)*indole* (**27**). A soln of **26** (200 mg, 0.760 mmol) and Rose Bengal (30 mg) in MeOH (20 ml) was irradiated with a 200 W halogen lamp through a Pyrex filter for 3 hr in a flow of O_2 at 0°. After treatment with Me_2S (0.5 ml), the mixture was worked-up as for **18**. Purification by column chromatography on silica gel eluting with $CHCl_3$ gave the 1 : 1 epimeric mixture of **27** (183 mg, 81.5%) as a colourless syrup; IR $\nu_{max}^{CHCl_3}$ 3580, 3550 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ 1.47 and 1.53 (each 1.5H, each s, Me-8a), 2.52 (1H, d, J = 3 Hz, H-3), 2.53 (1H, d, J = 4.2 Hz, H-3), 3.04 and 3.33 (each 1.5H, each s, OMe), 4.18 and 4.70 (each 0.5H, each d, J = 17 Hz, NC<u>H</u>$_2$Ph), 4.43 (1H, s, NC<u>H</u>$_2$Ph), 4.83 (0.5H, t, J = 4.2 Hz, H-2), 4.90 (0.5H, t, J = 3 Hz, H-2), 6.13–7.50 (9H, m, 9 × ArH); MS *m/z* 311 $[M]^+$. (Found: C, 73.74; H, 6.80; N, 4.37%. Calc for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50%.)

4-*Formylquinoline* (**13**). A soln of **28** (392 mg, 2.47 mmol) and Rose Bengal (30 mg) in MeOH (20 ml) was irradiated with a halogen lamp through Pyrex filter for 3 hr in a flow of O_2 at 0°. After addition of Me_2S (0.5 ml), the mixture was stirred for 2 hr at room temp and then evaporated. The residue was dissolved in HOAc–THF–H_2O (3 : 2 : 2; 10 ml) and the mixture was stirred for 10 min at room temp and then poured into sat $NaHCO_3$ aq in order to neutralize. After extraction with $CHCl_3$, the extract was washed with H_2O and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by silica gel column chromatography. Elution with

$CHCl_3$ afforded **13** (63 mg, 16.3%) as a brownish syrup, whose UV, IR and NMR spectra were identical with those of the authentic sample.[10]

4-Acetylquinoline (**31**). Photo-oxygenation of **29** (118 mg, 0.682 mmol) using Rose Bengal (30 mg) followed by the successive treatments with Me_2S (0.5 ml) and then HOAc–THF–H_2O (3:2:2; 10 ml) was carried out as above. After working-up, the crude product was purified by column chromatography on silica gel eluting with $CHCl_3$ to give **31** (73 mg, 62.6%) as a brownish syrup, which was converted into the picrate. Recrystallization from EtOH afforded yellow crystals, m.p. 165–170° (dec) [lit.[19] m.p. 165–170° (dec)].

4-Benzoylquinoline (**32**). Photo-oxygenation of **30** (120 mg, 0.51 mmol) using Rose Bengal (30 mg) followed by treatments with Me_2S (0.5 ml) and HOAc–THF–H_2O (3:2:2; 10 ml) was carried out as for **13**. After working-up, the product was purified by column chromatography on silica gel eluting with $CHCl_3$ to give **32** (90 mg, 75.7%) as a syrup, whose picrate was recrystallized from EtOH to afford yellow crystals, m.p. 220° (lit.[20] m.p. 220°).

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