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OXIDATIVE COUPLING OF PHENOLS AND PHENOLIC ETHERS—III[1]

SYNTHESIS OF ERYSODIENONE LACTAM FROM AN N-PHENACYLINDOLINE

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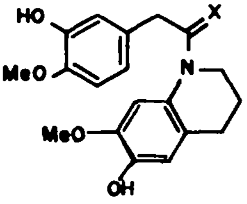
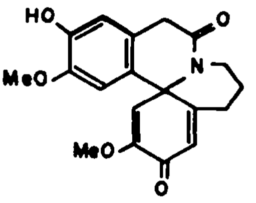
Abstract—The indoline (9) was prepared in high yield and converted into the diphenolic N-phenacylindoline (8). Ferricyanide oxidation of 8 gave erysodienone lactam (22) in 14% yield. This result is compared with earlier oxidations of 4 and 5.

Erysodienone (1), a key intermediate in the biosynthesis of the *Erythrina* alkaloids,[2] has been prepared[3,4] in >30% yield by ferricyanide oxidation of the bisphenethylamine (2). To define the course of this reaction Barton and Widdowson prepared the two possible stable intermediates (3 and 4) and subjected each one to the conditions of the oxidation reaction. The dibenzazonine (3) gave erysodienone (1) in 80% yield, whereas the N-phenethylindoline (4) gave no identifiable monomeric product.[5] The oxidation of the bisphenethylamine therefore follows the course 2→3→1.



5: X = O
7: X = H_2



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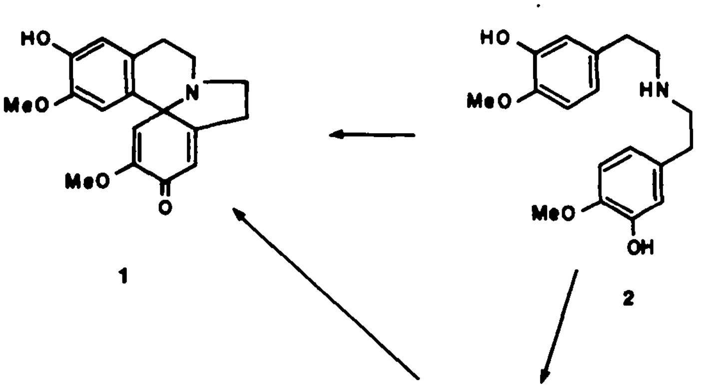
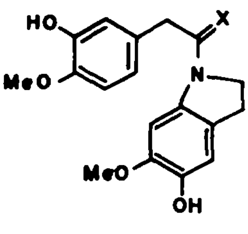
We have recently reported[1b] an efficient synthesis of the homoerysodienones via ferricyanide oxidation of the N-phenacyltetrahydroquinoline (5). Whereas 5 gave the lactam dienone (6) in 67% yield, the corresponding free base (7) gave on oxidation an intractable complex mixture.[1b] Clearly the design of the substrate molecule can be crucial in such oxidations and we therefore decided to investigate the amide (8), an analogue of indoline (4), as a potential synthetic precursor of the *Erythrina* and dibenz [d, f] azonine alkaloids.

For the synthesis of 8 we required the indoline (9) and this was prepared from 6-nitrohomoveratric acid[6] (10) in two ways. The first route 10→11→12→13→9, was

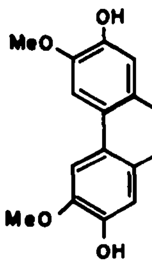


1

2



4: X = H_2
8: X = O



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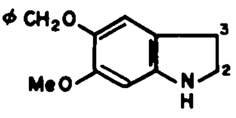
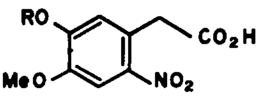
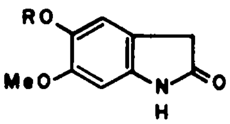


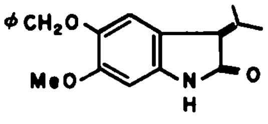
9
15: 2,3-dehydro
16: 1,2-dehydro



10: R = Me
11: R = H



12: R = H
13: R = $CH_2\phi$



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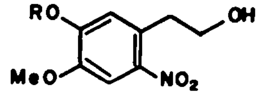
analogous to that followed in our earlier preparation[1b] of the tetrahydroquinoline (**5**).

In the O-benzylation of **12** many by-products were formed including the yellow acetone condensation-product (**14**) but after careful optimisation of conditions a 67% yield of **13** could be realised. The reduction of oxindole (**13**) to indoline (**9**) was achieved in 40% yield using diborane/THF but the required product had to be separated from the indole (**15**) which is probably formed by deprotonation of the intermediate (**16**). (The yield of **15** was unaltered when the reaction was run under N_2.)

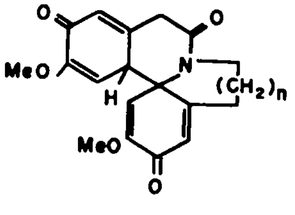


17: R = H
18: R = $CH_2\phi$

The second route avoided these two problems by effecting the corresponding steps at a different oxidation level of the side chain. Diborane reduction of the acid **11** gave alcohol **17**. Benzylation of **17** to give **18** proceeded without difficulty and reductive cyclisation of the mesylate (**19**) by Zn/HOAC then gave the required indoline (**9**) in 69% yield. This efficient indoline synthesis was modelled in the dimethoxy series and the intermediates are fully described in the Experimental.

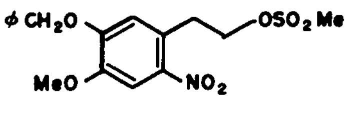
Indoline (**9**) was condensed with 3-benzyloxy-4-methoxy phenylacetic acid using DCC/CH_2Cl_2 to afford the N-acyl indole (**20**), an unstable compound easily autoxidised to the corresponding indole (**21**). Hydrogenolysis of **20** gave diphenol **8** and ferricyanide oxidation under carefully controlled conditions afforded erysodienone lactam **22** in 14% yield.

The yield in the oxidation step here is *ca* one-fourth that found[1a] for the homologous diphenol (**5**). At least some of the difference may be attributed to side reactions in which the indoline system is readily oxidised to the indole, but also molecular models suggest that there is considerably more strain in intermediate **23** than in **24**



23: n = 2
24: n = 3

so that *inter*molecular coupling (leading to polymer) may be relatively more favourable for **8** than for **5**. However, compared with the negative result reported[5] for the oxidation of **4** under the same conditions, the 14% yield of erysodienone lactam (**23**) from **22** is encouraging and reinforces the view[1b] that substrate design is an important factor in oxidative phenolic coupling.



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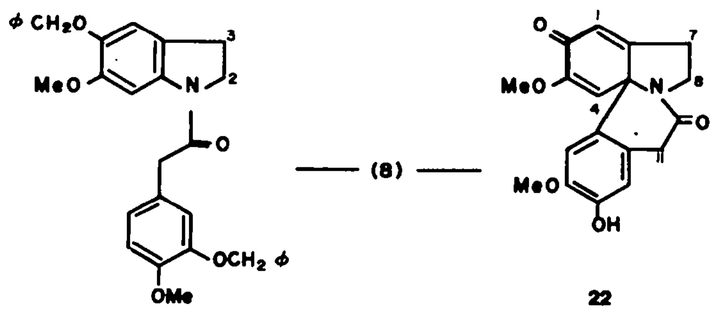
EXPERIMENTAL

For general instructions see Part I.[1a]

3,4-Dimethoxy-6-nitrobenzyl chloride. Freshly distilled $SOCl_2$ (1.9 ml) was added to a stirred soln of 3,4-dimethoxy-6-nitrobenzyl alcohol[7] (4.26 g) in dry CH_2Cl_2 (150 ml). After 1.5 hr, the mixture was evaporated *in vacuo* at 0° giving the title *chloride* as a pale yellow solid (3.4 g; 78%), m.p. 89–90° from cyclohexane. (Found: C, 46.56; H, 4.41; N, 6.4; Cl, 15.13. $C_9H_{10}ClNO_4$ requires: C, 46.6; H, 4.3; N, 6.0; Cl, 15.3%); ν_{max} (Nujol) 1613, 1578, 1515, 1320 cm^{-1}; λ_{max} 223, 244, 296, 342 nm. δ 4.0 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 5.05 (s, 2H, CH_2), 7.14 (s, 1H, H-2), 7.72 (s, 1H, H-5); *m/e* 233 (M^+, Cl = 37), 231 (M^+, Cl = 35), 216 (Cl = 37), 214 (Cl = 35), 188 (Cl = 37), 186 (Cl = 35).



20
21: 2,3-dehydro

22

This chloride was treated with KCN/DMF with a view to the preparation of 10 but the reaction was not a clean one.

3,4-*Dimethoxy-6-nitrophenylacetic acid* (10). Conc. HNO_3 was slowly added to a stirred soln of homoveratric acid (30 g) in glacial AcOH (200 ml) in a 3-necked flask immersed in an ice bath to prevent the temp. from rising about 65°. The mixture was allowed to stand at room temp. for 15 min. and was then poured into ice cold water. The ppt was collected, washed with water and dried giving 10 as pale yellow crystals (53 g, 86%) m.p. 206–207° from MeOH (lit.[6] m.p. 206–208°).

(Found: ν_{max} (Nujol) 3200–2600 (b), 1700, 1584, 1525, 1503, 1323 cm^{-1}; λ_{max} 215, 249, 298, 336 nm; δ (DMSO-d_6), 3.64 (s, 1H, OH), 3.90 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 3.97 (s, 2H, CH_2), 7.03 (s, 1H, H-2), 7.68 (s, 1H, H-5); *m/e* 241 (M^+).

3 - *Hydroxy - 4 - methoxy - 6 - nitrophenylacetic acid* (11). The foregoing acid 10; (40 g) was heated under reflux in 20% KOH aq (800 ml) for 45 hr. The red soln was allowed to cool and then poured into ice-water. The soln was acidified to pH1, the product collected, washed with H_2O and dried giving 11 as yellow needles (32.3 g, 86%) m.p. 193–194° from MeOH (lit.[8] 192°).

ν_{max} (Nujol) 3380, 3200–2600 (b), 1710, 1575, 1520, 1503, 1325 cm^{-1}; λ_{max} 205, 220, 247, 310, 345 changing with ^-OH to 273, 413 nm; δ (DMSO-d_6) 3.5 (b, 2H, exchanged with D_2O, OH), 3.85 (s, 2H, CH_2), 3.89 (s, 3H, OCH_3), 6.84 (S, 1H, H-2), 7.68 (s, 1H, H-5); *m/e* 227 (M^+), 210 (M^+–OH).

5-Hydroxy-6-methoxyoxindole (12). A mixture of the foregoing phenol (9 g), 10% Pd/C (900 mg) and glacial AcOH (150 ml) was shaken under H_2 at 40 psi at 80° for 4 hr. Filtration and evaporation gave *5-hydroxy-6-methoxyoxindole* (12) as an off-white solid (6.5 g, 92%) m.p. 219–221° from MeOH.

(Found: C, 59.93; H, 5.16; N, 8.08. $C_9H_9NO_3$ requires: C, 60.3; H, 5.0; N, 7.8%); ν_{max} (Nujol) 3340, 3180, 1685, 1600, 1500 cm^{-1}; λ_{max} 218, 268, 295 nm. δ (DMSO-d_6) 3.32 (s, 2H, CH_2), 3.79 (s, 3H, OCH_3), 3.2–4.0 (b, 2H, exchanged with D_2O, NH, OH), 6.48 (s, 1H, ArH), 6.72 (s, 1H, ArH); *m/e* 179 (M^+), 164 (M^+–CH_3).

5-Benzyloxy-6-methoxyoxindole (13). Benzyl chloride (1.9 g; 15 mmole) was added to a mixture of 12 (0.9 g), anhyd. K_2CO_3 (1.04 g) and NaI (2.25 g) in dry acetone and the mixture was refluxed under N_2 for 27 hr. Filtration and evaporation gave a dark red gum, which was dissolved in $CHCl_3$ and washed with Na_2CO_3 aq, H_2O, brine, then dried over Na_2SO_4 and thoroughly evaporated *in vacuo* (water pump then oil pump, 60°) giving a slurry (1.45 g) containing benzyl iodide and other impurities. These were removed by washing with ice-cold Et_2O (×3) leaving *5-benzyloxy-6-methoxyoxindole* (13) after recrystallization as colourless needles (0.91 g, 67%) m.p. 169–171° from EtOH.

(Found: C, 71.39; H, 5.91; N, 4.89. $C_{16}H_{15}NO_3$ requires: C, 71.4; H, 5.6; N, 5.2%); ν_{max} (Nujol) 3400 (b), 1695, 1625, 1500 cm^{-1}; λ_{max} 208, 250 nm; δ 3.44 (s, 2H, CH_2), 3.87 (s, 3H, OCH_3), 5.08 (s, 2H, PhCH_2), 6.55 (s, 1H, ArH), 6.84 (s, 1H, ArH), 7.38 (m, 5H, PhH), 8.83 (b, 1H, exchanged with D_2O, NH); *m/e* 269 (M^+), 178 (M^+–C_7H_7).

The yield quoted above was not easily reproduced, and was frequently only 30–40%. From the ether washings a yellow solid was obtained by trituration with MeOH and identified by the following analytical and spectral data as 5 - *benzyloxy* - 3 - *isopropylidene* - 6 - *methoxyoxindole* (14) (yield *ca.* 6%), m.p. 203–205° from acetone. Found: C, 73.60; H, 6.32; N, 4.5. $C_{19}H_{19}NO_3$ requires: C, 73.7; H, 6.1; N, 4.6%); ν_{max} (Nujol) 3160, 1683, 1625, 1613, 1500 cm^{-1}; λ_{max} 270, 300 nm; δ 2.20 (s, 3H, vinyl OCH_3), 2.55 (s, 3H, vinyl CH_3), 3.90 (s, 3H, CH_3), 5.10 (s, 2H, PhCH_2, 6.50 (s, 1H, ArH), 7.10 (s, 1H, ArH), 7.40 (m, 5H, PhH); *m/e* 309 (M^+), 218 (M^+–91).

3,4 - *Dimethoxy* - 6 - *nitrophenethyl alcohol*. Conc. HNO_3 (4.83 ml) was added dropwise at 0° to a stirred soln of homoveratryl alcohol (3.02 g) in glacial AcOH (30 ml). The mixture was stirred for 1 hr at 20° and then added to ice-water. The solid which separated was collected, washed with H_2O, and dried giving 6-nitrohomoveratryl alcohol as yellow crystals (3.32 g, 88.1%) m.p. 106–107° from benzene–hexane (lit.[9], m.p. 107°). ν_{max} (Nujol) 3520, 3200–3400 (b), 1610, 1580, 1520, 1330 cm^{-1}; δ 1.84 (s, 1H, OH), 3.18 (t, 2H, J = 6Hz, ArCH_2), 3.92 (t, 2H, CH_2O), 3.90 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 6.78 (s, 1H, H-2), 7.57 (s, 1H, H-5); *m/e* 227 (M^+) 196 (M^+–OCH_3). This method is a considerable improvement on the literature procedure.

3 - *Hydroxy* - 4 - *methoxy* - 6 - *nitrophenethyl alcohol* (17). $BF_3 \cdot Et_2O$ (2.2 ml, 12.5 mmole) was added dropwise to a mixture of 11 (1.13 g) and $NaBH_4$ (0.47 g) in dry THF (25 ml) at 0° under N_2. The mixture was then stirred at 20° for 3 hr, cooled to 0°, and quenched with 10% NaOH aq. The soln was neutralised to *ca.* pH = 6 and the THF removed *in vacuo.* The solid which separated was collected, washed with H_2O and dried giving *3-hydroxy-4-methoxy-6-nitrophenethylalcohol* (17) as a pale yellow solid (0.96 g, 92%), m.p. 145–146° from $CHCl_3$. (Found: C, 50.51; H, 5.24; N, 6.65. $C_9H_{11}NO_5$ requires: C, 50.7; H, 5.2; N, 6.6%); ν_{max} (Nujol) 3560–3100 (b), 1580, 1525, 1330 cm^{-1}; λ_{max} 215, 246, 305, 347 nm; δ (DMSO-d_6), 2.97 (t, 2H, J = 7Hz, ArCH_2), 3.62 (t, 2H, CH_2OH), 3.84 (s, 3H, OCH_3), 3.89 (b, 1H, exchanged with D_2O, ROH), 6.82 (s, 1H, H-2), 7.56 (s, 1H, H-5), 10.31 (b, 1H, exchanged with D_2O, Ph–O*H*); *m/e* 213 (M^+), 197 (M^+–CH_3), 182 (M^+–OCH_3), 178, 166, 151.

3 - *Benzyloxy* - 4 - *methoxy* - 6 - *nitrophenethanol* (18). A mixture of 17 (1.12 g) anhyd K_2CO_3 (0.406 g), benzyl chloride (0.789 g) in dry DMF (7 ml) was stirred under N_2 at 110° for 6 hr, cooled to 20° and then added to an ice-water mixture. The solid which separated out was collected, washed with H_2O, dried and recrystallized giving 3 - *benzyloxy* - 4 - *methoxy* - 6 - *nitrophenethyl alcohol* (18) as pale yellow needles (1.42 g, 89%) m.p. 99–100° from benzene–hexane. (Found: C, 63.16; H, 5.66; N, 4.36. $C_{16}H_{17}NO_5$ requires: C, 63.4; H, 5.6; N, 4.6%); ν_{max} (Nujol) 3200–3650 (b), 1610, 1575, 1520, 1340 cm^{-1}; λ_{max} 215, 245, 300, 345 nm. δ 1.68 (s, 1H, OH), 3.12 (t, 2H, J = 6Hz, ArCH_2), 3.86 (t, 2H, CH_2OH), 3.90 (s, 3H, OCH_3), 5.21 (s, 2H, PhCH_2), 6.83 (s, 1H, H-2), 7.59 (s, 1H, H-5), 7.38 (m, 5H, PhH); *m/e* 303 (M^+), 253, 162, 135.

3 - *Benzyloxy* - 4 - *methoxy* - 6 - *nitrophenethyl* - *mesylate* (19). Mesyl chloride (0.458 g) was added to a soln of 18 (1.01 g) and Et_3N (0.505 g) in dry CH_2Cl_2 (15 ml) at 0° under N_2. The mixture was stirred at 0° for 15 min and then at room temp. for a further 15 min. Work up, which included washing with H_2O, dil. HCl, $NaHCO_3$ aq, brine, drying over Na_2SO_4, evaporation and recrystallization gave *mesylate* (19) as yellow crystals (1.15 g, 90.5%) m.p. 125–126° from benzene–hexane. (Found: C, 53.54; H, 5.09; N, 3.64; S, 8.29. $C_{17}H_{19}NO_7S$ requires: C, 53.5; H, 5.0; N, 3.7; S, 8.4%); ν_{max} (Nujol) 1620, 1580, 1525, 1325 cm^{-1}; λ_{max} 217, 244, 298, 340 nm; δ 2.88 (s, 3H, SO_3CH_3), 3.30 (t, 2H, J = 6Hz, ArCH_2), 3.91 (s, 3H, OCH_3), 4.48 (t, 2H, CH_2OS), 5.22 (s, 2H, PhCH_2), 6.87 (s, 1H, H-2), 7.64 (s, 1H, H-5), 7.39 (m, 5H, PhH); *m/e* 318 (M^+), 285 (M^+–$MeSO_3H$).

3,4 - *Dimethoxy* - 6 - *nitrophenethyl mesylate*. 6-Nitrohomoveratryl alcohol (0.45 g), mesyl chloride (0.18 ml) and Et_3N (0.30 g) in dry CH_2Cl_2 (10 ml) were reacted as above to give *6-nitrohomoveratryl mesylate* (0.52 g, 85%) m.p. 106–107° from benzene–hexane. (Found: C, 43.38; H, 4.92; N, 4.50; S, 10.26. $C_{11}H_{15}NO_7S$ requires: C, 43.2; H, 4.9; N, 4.6; S, 10.5%); IR (Nujol) 1615, 1575, 1525, 1500 cm^{-1}; UV 220, 244, 295, 340 nm; NMR 2.96 (s, 3H, SO_2Me), 3.39 (t, 2H, J = 6Hz, ArCH_2), 3.94 (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 4.55 (t, 2H, CH_2OMes), 6.82 (s, 1H, H-2), 7.64 (s, 1H, H-5); *m/e* 305 (M^+) 210 (M^+–OSO_2Me).

5 - *Benzyloxy* - 6 - *methoxy* - 2,3 - *dihydroindole* (9)

(a) *From oxindole* (13). $BF_3 \cdot Et_2O$ (2.56 g) was added dropwise to a stirred mixture of $NaBH_4$ (0.732 g) and 13 (0.807 g) in dry THF (180 ml) at 0° under N_2. The mixture was then stirred at 20° for 7 days. Work up by careful addition of 10% NaOH aq, extraction with $CHCl_3$, washing the combined $CHCl_3$ extracts with H_2O, brine, drying over Na_2SO_4 and evaporating *in vacuo* gave an oil to which oxalic acid (0.375 g) in MeOH was added. The oxalate salt of 9 was collected after addition of Et_2O to the methanolic soln and recrystallized to give the pure *oxalate salt of* 9 as needles (0.409 g, 39%), m.p. 169–170° from MeOH–Et_2O. (Found: C, 62.57; H, 5.61; N, 4.03. $C_{18}H_{19}NO_6$ requires: C, 62.6; H, 5.5; N, 4.0%); ν_{max} (Nujol) 2700–3500 (b), 1700, 1600, 1580, 1505 cm^{-1}; λ_{max} 213, 237, 300. δ (DMSO-d_6), 2.9 (t, 2H, J_{23} = 8Hz, H_3), 3.49 (t, 2H, H-2), 3.76 (s, 3H, OCH_3), 4.95 (s, 2H, PhCH_2), 6.45 (s, 1H, ArH), 6.81 (s, 1H, ArH), 7.37 (m, 5H, PhH), 7.7 (b, 3H, exchanged with D_2O, NH, OH); *m/e* 255 (M^+), 254 (M^+–H), 164.

The mother liquors were combined and evaporated. The residue purified by preparative tlc (SiO_2, Et_2O) gave starting material

13 (24 mg, R_f 0.4) and 15 (48 mg, R_f 0.9); ν_{max} ($CHCl_3$) 3490, 1630, 1510 cm^{-1}; λ_{max} 209, 260, 297 nm. δ 3.83 (s, 3H, OCH_3), 5.24 (s, 3H, Ph*CH*$_2$), 6.37 (m, 1H, collapses to a doublet on D_2O shake, J_{23} = 3Hz, H-3), 6.98 (dd, 1H, J_{12} = 2Hz, J_{23} = 3Hz, H-2); *m/e* 253 (M^+), 252 (M^+–H) 162.

(b) *From nitromesylate* (19). Compound 19 (190 mg) was added slowly to a vigorously stirred slurry of Zn (0.65 g) in glacial AcOH (10 ml) under N_2. After the addition was complete the mixture was stirred at 20° for a further 30 min. Filtration and evaporation *in vacuo* gave a yellow oil which was dissolved in CH_2Cl_2 and washed with dil HCl (×3). The acidic washings were neutralized and back extracted with CH_2Cl_2. The combined organic extracts were washed with H_2O, brine, dried over Na_2SO_4 and evaporated leaving 9 (63 mg, 50%).

5,6 - *Dimethoxy - 2,3 - dihydroindole* 6 - Nitrohomoveratryl mesylate (150 mg) and Zn (0.65 g) in glacial AcOH (10 ml) were reacted as above to give the indoline (46 mg, 52%) characterised as the *oxalate* m.p. 172–174° from MeOH–Et_2O. (Found: C, 53.48; H, 5.25; N, 5.43. $C_{12}H_{15}NO_6$ requires: C, 53.5; H, 5.5; N, 5.2%).

1 - (3' - *Benzyloxy - 4' - methoxy) phenylacetyl - 5 - benzyloxy - 6 - methoxy - 2,3 - dihydroindole* (20). A soln of DCC (229 mg) in dry CH_2Cl_2 (3 ml) was added to a stirred soln of 9 (254 mg) and 3-benzyloxy-4-methoxy phenyl acetic acid (328 mg) in dry CH_2Cl_2 (7.5 ml) under N_2 at 0°. After 30 min the mixture was allowed to warm to 20° and it was then stirred at this temp. for 18 hr. The mixture was filtered through celite, diluted with CH_2Cl_2, washed with sat Na_2CO_3 aq, H_2O, brine, dried (Na_2SO_4) and evaporated to give *phenacylindoline* (20) as an air sensitive solid (0.42 g, 83%) m.p. 131–134° from MeOH. (Found: C, 74.9; H, 6.55; N, 2.65. $C_{32}H_{31}NO_5$ requires: C, 75.4; H, 6.1; N, 2.75%); ν_{max} (Nujol) 1660, 1610, 1590, 1495 cm^{-1}; λ_{max} (MeOH) 263, 304 nm; δ 2.90 (t, 2H, J = 9Hz, H-3), 3.75 (t, 2H, H-2), 3.70 (s, 2H, Ar*CH*$_2$CO), 3.90 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 5.12 (s, 2H, Ph*CH*$_2$), 5.20 (s, 2H, Ph*CH*$_2$), 6.70–7.0 (m, 4H, ArH), 7.2–7.7 (m, 10H, PhH), 8.11 (s, 1H, H_7); *m/e* 509 (M^+), 418 (M^+–C_7H_7).

1 - (3' - *Hydroxy - 4' - methoxy) phenylacetyl - 5 - hydroxy - 6 - methoxy - 2,3 - dihydroindole* (8). A mixture of the amide (200 mg) and 10% Pd/C (40 mg) in $CHCl_3$ (0.6 ml), MeOH (3.2 ml) and MeOH/HCl (5 drops) was hydrogenated at 20° for 1.5 hr. The mixture was filtered through Celite and evaporated giving 8 as an unstable oil (10% mg, 83%), 1 spot on tlc (SiO_2, EtOAc–5% MeOH); ν_{max} ($CHCl_3$) 3540, 3100–3400 (b), 1645, 1615, 1590, 1490 cm^{-1}, λ_{max} (MeOH) 265, 305 changing in $^-$OH to 283, 317 nm; δ 3.00 (t, 2H, J_{23} = 9Hz, H-3) 3.65 (s, 2H, Ar*CH*$_2$CO), 3.81 (s, 6H, OCH_3), 4.01 (t, 2H, H-2), 5.7 (b, 2H, exchanged with D_2O, .OH), 6.65–6.90 (m, 4H, ArH), 7.98 (s, 1H, ArH); *m/e* 329 (M^+).

10-*Oxo-erysodienone* (22). A degassed soln of 8 (50 mg) in $CHCl_3$ (5 ml) was added to a degassed two phase system consisting of $CHCl_3$ (70 ml) and 5% $NaHCO_3$ aq (17 ml) containing $K_3Fe(CN)_6$ (500 mg, 4 eq.) and the mixture was stirred for 19 hr at such a rate that the vortex of the aqueous layer just touched the bottom of the flask and there was still a clean separation between the two phases. The aqueous layer was acidified to *ca.* pH6 and the $CHCl_3$ layer removed. The aqueous layer was extracted with $CHCl_3$ and the combined organic extracts were washed with H_2O, brine, dried (Na_2SO_4), filtered through Celite and evaporated leaving 33 mg, which was eluted through a silica column with $CHCl_3$ to give 24 mg and then purified by preparative tlc (SiO_2, EtOAc/5% MeOH) to give *10-oxoerysodienone* (22) as a gum (7 mg, 14.1%). (Found: M^+, 327.1093. $C_{18}H_{17}NO_5$ requires: 327.1106); ν_{max} ($CHCl_3$) 3540 (b), 1680, 1655, 1620 cm^{-1}, λ_{max} (MeOH) 211, 233, 280 nm; δ 2.77–2.53 (m, 2H, H-7), 3.58 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.51–3.88 (m, 3H, H-11(2H), H-8(1H), hidden under MeO signals), 4.31–4.62 (m, 1H, H-8), 5.98 (s, 1H, H-4), 6.53 (s, 2H, ArH), 6.78 (s, 1H, H-1), 5.61–5.79 (b, 1H, exchanged with D_2O, OH); *m/e* 327 (M^+).

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