Synthesis of 1,12b-Didehydrolycoran (α-Anhydrodihydrocaranine) and 12bα-Lycoran (γ-Lycoran) *via* Photocyclisation of an Enamide-ketone

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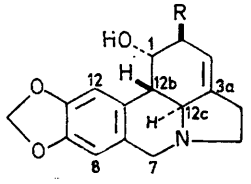
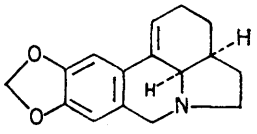
A novel stereoselective synthesis of lycorine-type alkaloids from a key intermediate obtained by photocyclisation of an enamido-ketone is described. Birch reduction of 6-methoxyindoline, prepared by a benzyne reaction of 3-chloro-4-methoxyphenethylamine, gave 3,3a,4,5-tetrahydro-6-methoxy-2*H*-indole (18) which reacted with benzoyl and 3,4-methylenedioxybenzoyl chloride to form the corresponding *N*-acylindol-6-one derivatives (20) and (21). Irradiation of both enamido-ketones yielded, respectively, the pyrrolo[3,2,1-*de*]phenanthridine derivatives (22) and (23). The latter (23), on treatment with lithium aluminium hydride, was stereoselectively converted into (±)-1,12b-didehydrolycoran (3), which was then hydrogenated to (±)-12bα-lycoran (5).

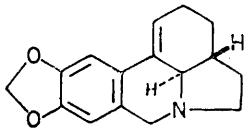
ALTHOUGH Amaryllidaceae alkaloids of the lycorine (1) type have not yet been totally synthesised, in studies directed towards the synthesis of these alkaloids several routes to related compounds, possessing the pyrrolo[*de*]-phenanthridine skeleton, derived from natural sources have been developed. Dehydration of α-[1,2] and β-dihydrocaranine,[2,3] derived from lycorine (1) or caranine (2), affords respectively α- and β-anhydrodihydrocaranine [(3) [1,4] and (4) [4]], the former of which can be hydrogenated



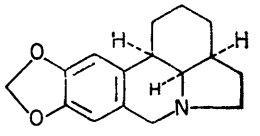
(1) R=OH
(2) R=H



(3)



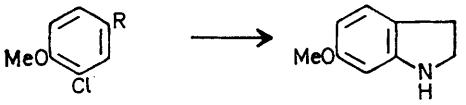
(4)



(5)

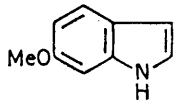
to γ-lycoran (5),[4] one of the four possible stereoisomers of lycoran. Of these compounds, γ-lycoran has been elaborated by several groups,[5] but there have been no reports on the synthesis of dihydrocaranine and anhydrodihydrocaranine. We hoped to develop simple and convenient routes to these lycorine-type compounds, and describe here an efficient photocyclisation of enamido-ketones,[6] and its application to the novel stereo-selective synthesis (±)-α-anhydrodihydrocaranine (1,12b-didehydrolycoran) (3) and (±)-γ-lycoran (12bα-lycoran) (5).

Chlorination of *p*-anisaldehyde with sulphuryl chloride and reaction of the product (6) with nitromethane in acetic acid in the presence of ammonium acetate gave the nitrostyrene (7). Reduction of this with lithium aluminium hydride to give the phenethylamine (8), followed by ring closure involving a benzyne reaction with phenyl-lithium and diethylamine in ether, afforded 6-methoxyindoline (9) (42%) together with a minor amount of 6-methoxyindole (10) (5%). Acylation of the



(6) R=CHO
(7) R=CH:CH·NO$_2$
(8) R=CH$_2$CH$_2$NH$_2$

(9)
+



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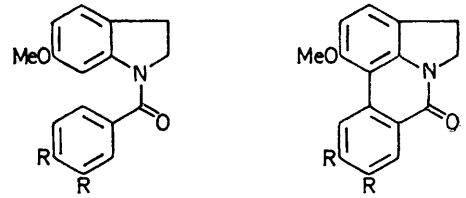
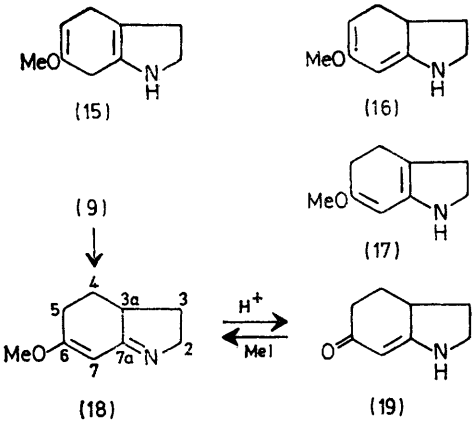


(11) R=H
(12) RR=O·CH$_2$O

(13) R=H
(14) RR=O·CH$_2$O

indoline (9) with benzoyl and 3,4-methylenedioxybenzoyl chloride gave the amides (11) and (12), respectively.



(15)

(16)

(9)

(17)

(18)

(19)

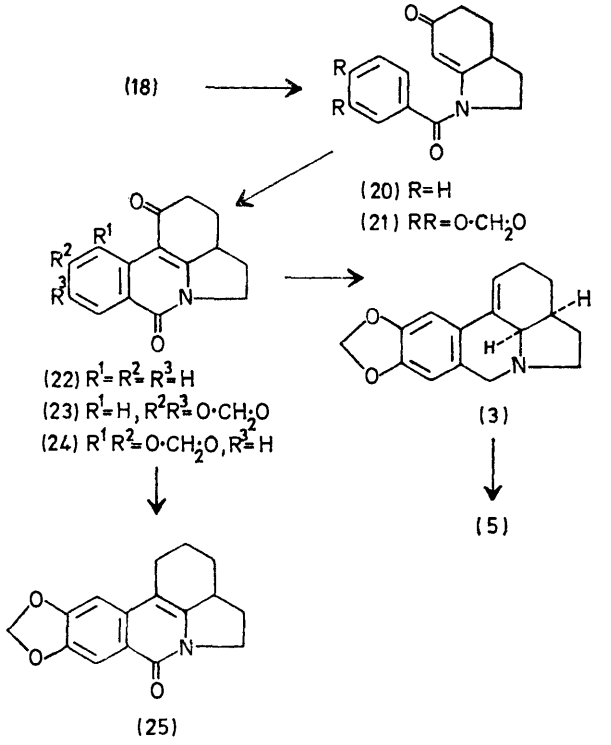
Attempted photocyclisation of both amides (11) and (12) to form the corresponding anhydrolycorines (13) and (14)

[1] K. Takeda and K. Kotera, *Chem. and Ind.*, 1956, 347; *Chem. and Pharm. Bull. (Japan)*, 1957, **5**, 234.
[2] E. W. Warnfoff and W. C. Wildman, *J. Amer. Chem. Soc.*, 1957, **79**, 2192.
[3] K. Kotera, *Tetrahedron*, 1961, **12**, 240.
[4] K. Kotera, *Tetrahedron*, 1961, **12**, 248.
[5] (*a*) N. Ueda, T. Tokuyama, and T. Sakan, *Bull. Chem. Soc. Japan*, 1966, **39**, 2012; (*b*) H. Irie, Y. Nishitani, M. Sugita, and S. Uyeo, *Chem. Comm.*, 1970, 1313; (*c*) B. Ganem, *Tetrahedron Letters*, 1971, 4105.
[6] I. Ninomiya, T. Naito, and T. Kiguchi, *J.C.S. Perkin I*, 1973, 2257.

(irradiation with a low pressure mercury lamp for 70 h) resulted in no reaction in each case.

We next turned our attention to the enamido-ketones (20) and (21) as precursors; these compounds were expected to be more sensitive to irradiation and also have an advantage in that cyclisation would afford a lycorine skeleton including a dearomatised ring c.

The synthesis of compounds (20) and (21) began with Birch reduction of 6-methoxyindoline (9) with lithium in liquid ammonia and tetrahydrofuran in the presence of methanol to afford a single product in excellent yield.



Either the unconjugated diene structure (15) or the dienamine structure (16) would be expected for this product by analogy with Birch's work,[7] but the ^{1}H n.m.r. spectrum ruled out these structures, showing an olefinic proton signal as a sharp singlet at δ 5.62 indicating the lack of a vicinal proton. On this basis, in the preliminary communication [8] we reported that the product might be represented by the isomeric formula (17). However, the u.v. absorption ($\lambda_{max.}$ 242.5 nm) indicated the presence of a conjugated azomethine chromophore, suggesting that the product existed in the tautomeric imino-form (18). To obtain the unambiguous proof of the location of the unsaturation, the ^{13}C n.m.r. spectrum (see Table) was examined. The spectrum revealed the presence of the three sp^2-hybridised carbon atoms (δ 95.0, 169.7, and 175.1) of which two gave rise to singlets, indicating the lack of an attached proton. This observation excluded structure (17) and agreed with the imino-enol ether structure (18). Chemical evidence for structure (18) was provided by an alternative synthesis. The Birch reduction product was treated with hydrochloric acid to give the enamino-ketone (19), identified on the basis of spectral and analytical data (see Experimental section). It has been reported that enamino-ketones can be converted into imino-enol ethers by treatment with alkyl iodides.[9]

^{13}C N.m.r. data for the imino-enol ether (18) [a]

Carbon no.	2	3 5	4	3a	6-OMe	6 7a	7
δ [b] (multiplicity [c])	59.7 (t)	29.4 * (t) 30.5 * (t)	28.0 (t)	45.5 (d)	55.1 (q)	169.7 * (s) 175.1 * (s)	95.0 (d)

[a] Solution in deuteriochloroform. [b] Internal standard tetramethylsilane. [c] Obtained from the off-resonance spectrum.
* Assignments of these pairs of chemical shifts cannot be made with confidence.

Accordingly, prolonged heating of the enamino-ketone (19) with a large excess of methyl iodide furnished the corresponding imino-enol ether (18), whose i.r. and ^{1}H n.m.r. spectra and t.l.c. behaviour agreed with those of the specimen prepared by Birch reduction of the indoline.

Treatment of the imino-enol ether (18) with benzoyl chloride in the presence of aqueous alkali resulted in *N*-acylation with de-*O*-methylation *in situ* to give the enamido-ketone (20). Similarly, reaction of the imino-enol ether (18) with 3,4-methylenedioxybenzoyl chloride gave the enamido-ketone (21). Each structure was confirmed by analytical and spectral data; the enamido-ketone chromophore was characterised by the u.v. [$\lambda_{max.}$ 292 nm (20); and 300 nm (21)] and i.r. spectra [$\nu_{max.}$ 1 670, 1 642, and 1 602 cm^{-1} (20); and 1 667, 1 642, and 1 606 cm^{-1} (21)]. The ^{1}H n.m.r. spectra of compounds (20) and (21) each showed an olefinic one-proton singlet, at δ 6.26 and 6.37, respectively.

Irradiation of the two enamido-ketones (20) and (21) in either dichloromethane or tetrahydrofuran with a low pressure mercury lamp for 12 h gave the corresponding dehydrogenated photoproducts (22) (69%) and (23) (70%), respectively. When a 100 W high pressure mercury lamp was used to irradiate the enamido-ketone (21) the reaction proceeded more smoothly and was complete in 1 h to afford the photoproduct (23) (70%). Stereomodels indicate that the alternative mode of cyclisation of the enamido-ketone (21) to the structural isomer (24) is not sterically favoured because of serious non-bonded interaction between the 1-carbonyl group and the 11-ether oxygen atom. Hence the reaction appears to proceed regioselectively to give the cyclised compound (23) as sole product. Compound (23) was identified on the basis of the ^{1}H n.m.r. spectrum, which showed signals for two aromatic protons at δ 7.67 and 8.62 as a pair of singlets instead of the AB-type quartet expected for the isomer (24). In addition, one of these singlets, attributed to the C-11 proton (δ 8.62), was at lower field than the other owing to the proximity of this proton to the 1-carbonyl group. The same effect was observed for the C-11 proton in compound (22) [δ 9.22 (dd, *J* 8 and 2 Hz)]. Verification of the structure (23) was provided by comparison [m.p. and u.v. absorption maxima (see Experimental section)] with data reported for authentic samples derived from natural lycorine (1) [1] or caranine (2).[2]

[7] A. J. Birch, E. G. Hutchinson, and G. S. Rao, *J. Chem. Soc.* (*C*), 1971, 637.
[8] H. Iida, S. Aoyagi, and C. Kibayashi, *J.C.S. Chem. Comm.*, 1974, 499.
[9] N. J. Leonard and J. A. Adamcik, *J. Amer. Chem. Soc.*, 1959, **81**, 595; C. A. Grob and H. J. Wilkens, *Helv. Chim. Acta*, 1967, **50**, 725.

Hydrogenation of the photoproduct (23) over Adams catalyst in acetic acid gave the deoxygenated product (25) *via* hydrogenolysis of the intermediate alcohol. The C-11 proton signal (δ 6.87) of the product (25) was markedly shifted upfield (by 1.75 p.p.m.) in comparison with the oxo-lactam (23), probably owing to the lack of deshielding by a proximate 1-oxo-group. Further support for structure (25) was obtained from its u.v. spectrum (see Experimental section), which was closely similar to that reported for an isoquinolin-1-one homologue,[10] a degradation product of lycorine. Attempts to convert compound (25) into the lycoran (5) by catalytic reduction in acidic media or with lithium aluminium hydride were not successful: most of the starting material was unchanged or a complex mixture of unidentified products was obtained, respectively.

On the other hand, treatment of the photoproduct (23) with lithium aluminium hydride in tetrahydrofuran gave (±)-α-anhydrodihydrocaranine (3) in 32% yield. Assignment of the stereochemistry of the product was based on its u.v. absorption maxima [263 (log ε 4.11) and 310 nm (3.86)], which agreed with those reported for the (−)-α-isomer (3) [263 (4.12) and 310 (3.84)] [4] but not with those for the (−)-β-isomer (4) [266 (4.20) and 3.12 (3.85)].[4] Additional evidence for this assignment was provided by the n.m.r. spectrum, in which the 12c-H–3a-H coupling constant was 7.5 Hz, thus proving that the CD ring junction is *cis*. Finally, hydrogenation of compound (3) over Adams catalyst in acetic acid gave (±)-γ-lycoran (5) in 47% yield; the m.p. (102—104°) of the product was consistent with that reported,[5b] and its i.r. spectrum (in carbon disulphide) was identical with that of an authentic sample.

EXPERIMENTAL

U.v. spectra were measured for solutions in ethanol with a Hitachi 124 spectrophotometer. I.r. spectra were taken with a Hitachi 215 grating spectrophotometer (for solutions in chloroform unless otherwise stated). ^{1}H N.m.r. spectra were recorded with a Varian T-60 (60 MHz) or a JEOL JNM-PS-100 (100 MHz) spectrometer, with deuteriochloroform as solvent and tetramethylsilane as internal standard. ^{13}C N.m.r. spectra were determined at 15.1 MHz with a Varian NV-14 instrument. Mass spectra were taken with a Hitachi RMU-7L double-focusing spectrometer (ionising voltage 70 eV). T.l.c. was carried out on precoated plates of Merck silica gel 60 F_{254}.

3-Chloro-4-methoxybenzaldehyde (6).—Sulphuryl chloride (238 g, 1.76 mol) was added during 30 min with stirring to *p*-anisaldehyde (200 g, 1.47 mol) containing pyridine (3 ml). After the reaction had subsided, the mixture was stirred at 60 °C for 2.5 h, and the volatile material was evaporated off *in vacuo* at room temperature to leave an oil which solidified. The solid was washed with water and recrystallised from ether–hexane to give needles (191.5 g, 76.4%), m.p. 62—63° (lit.,[11] 62.5—63°).

3-Chloro-4-methoxy-β-nitrostyrene (7).—A solution of the aldehyde (6) (155 g, 0.91 mol) and nitromethane (80 g, 1.31 mol) in acetic acid (300 ml) was stirred at 100° C for 2 h. The hot mixture was left overnight after addition of water (30 ml). Collection of the resulting crystals followed by washing with methanol gave the *nitrostyrene* (7) (128 g, 65.9%) as yellow needles, m.p. 103—104° (from methanol) (Found: C, 50.55; H, 3.7; N, 6.9. $C_9H_8ClNO_3$ requires C, 50.6; H, 3.8; N, 6.55%); $\nu_{max.}$ 1 628 (C=C) and 1 332 cm^{-1} (NO_2) (no C=O band).

3-Chloro-4-methoxyphenethylamine (8).—The nitrostyrene (7) (220 g) in dry tetrahydrofuran (1 l) was added dropwise to a stirred ice-cold suspension of lithium aluminium hydride (165 g) in tetrahydrofuran (1 l), the temperature of the mixture not being allowed to exceed 15 °C. The solution was then stirred at room temperature for 5 h, decomposed at 0 °C by addition of ethyl acetate followed by ice-cold aqueous 30% sodium hydroxide, and filtered through Celite. The filtrate was dried (K_2CO_3) and evaporated to leave an oil which was distilled *in vacuo* to give the phenethylamine (8) (115 g, 60.2%) as an oil, b.p. 84° at 0.05 mmHg (lit.,[12] 165° at 15 mmHg); $\nu_{max.}$ (neat) 3 360 and 3 265 cm^{-1} (NH_2); δ 1.60 (2 H, s, NH_2), 2.48—3.05 (4 H, m, $[CH_2]_2$), 3.89 (3 H, s, OMe), 6.84 (1 H, d, *J* 9 Hz, 5-H), 7.08 (1 H, dd, $J_{5,6}$ 9, $J_{2,6}$ 2 Hz, 6-H), and 7.20 (1 H, d, *J* 2 Hz, 2-H).

Benzyne Reaction of 3-Chloro-4-methoxyphenethylamine (8).—To a solution of the phenethylamine (8) (22.4 g, 0.12 mol) and diethylamine (8.8 g, 0.12 mol) in dry ether (200 ml) was added phenyl-lithium [from bromobenzene (0.4 mol) and lithium (0.8 mol)] in dry ether (400 ml), and the mixture was refluxed with stirring for 20 h under nitrogen. After cooling, the ethereal solution was washed with ice-cold water, dried (K_2CO_3), and evaporated to leave an oil which was chromatographed on alumina. Elution with benzene gave an oil which was dissolved in absolute ethanol and converted into the hydrochloride by treatment with saturated ethanolic hydrogen chloride followed by dry ether. The crystalline precipitate was filtered off, washed with ether, and recrystallised from ethanol to give *6-methoxyindoline* (9) *hydrochloride* (8.8 g) as leaflets, m.p. 223—224° (Found: C, 58.1; H, 6.5; N, 7.75. $C_9H_{12}ClNO$ requires C, 58.3; H, 6.45; N, 7.55%). The oily free base had $\nu_{max.}$ (neat) 3 370 cm^{-1} (NH); δ 2.93 (2 H, m, 3-H_2), 3.50 (2 H, m, 2-H_2), 3.75 (3 H, s, OMe), 3.82 (1 H, s, NH), 6.25 (1 H, d, *J* 2 Hz, 7-H), 6.27 (1 H, dd, $J_{4,5}$ 9, $J_{5,7}$ 2 Hz, 7-H), and 7.02 (1 H, d, *J* 9 Hz, 4-H).

Continued elution with benzene–chloroform (1 : 1) gave an oil, which was rechromatographed on silica gel (15 g) with benzene as eluant. The first-eluted material was a further crop of the indoline (9) [total yield (as the hydrochloride) 9.38 g, 41.9%]. The second-eluted material was recrystallised from ether–hexane to give 6-methoxyindole (10) (0.92 g, 5.2%), m.p. 90—92° (lit.,[13] 91—92°); $\nu_{max.}$ 3 390 cm^{-1} (NH); δ 3.83 (3 H, s, OMe), 6.42—7.07 (4 H, m, aromatic), and 7.53 (1 H, d, *J* 9 Hz, 4-H).

N-Acylation of 6-Methoxyindoline (9).—(*a*) A solution of benzoyl chloride (1.6 g) in chloroform (15 ml) was added to a solution of 6-methoxyindoline (9) (1.6 g) and pyridine (10 ml) in chloroform (15 ml) in an ice-bath. The solution was stirred at 5—10 °C for 1 h and washed with 2N-hydrochloric acid, 2N-potassium carbonate, and water. Drying ($MgSO_4$) and evaporation left an oil which solidified on trituration with ether. Recrystallisation from benzene–hexane gave N-

[10] S. Takagi, W. I. Taylor, S. Uyeo, and H. Yajima, *J. Chem. Soc.*, 1955, 4003.
[11] P. Pfeiffer and B. Segall, *Annalen*, 1928, 460.
[12] M. Juria and H. Gaston-Brenton, *Bull. Soc. chim. France*, 1966, 1335.
[13] W. O. Kermack, W. H. Perkin, jun., and R. Robinson, *J. Chem. Soc.*, 1921, 1602.

benzoyl-6-methoxyindoline (11) (2.0 g, 78%) as needles, m.p. 83—84° (Found: C, 76.0; H, 5.9; N, 5.2. $C_{16}H_{15}NO_2$ requires C, 75.85; H, 5.95, N, 5.55%); $\nu_{max.}$ 1 634 cm^{-1} (C=O).

(*b*) A solution of 3,4-methylenedioxybenzoyl chloride [from 3,4-methylenedioxybenzoic acid (1.5 g) and thionyl chloride (8 ml)] in chloroform (10 ml) was added to a solution of 6-methoxyindoline (9) (1.1 g) and pyridine (7 ml) in chloroform (10 ml) in an ice-bath. The solution was worked up as in (*a*). Recrystallisation from benzene–hexane gave N-(*3,4-methylenedioxybenzoyl*)-*6-methoxyindoline* (12) (1.5 g, 73%) as needles, m.p. 115—116° (Found: C, 68.85; H, 5.15; N, 4.65. $C_{17}H_{15}NO_4$ requires C, 68.65; H, 5.1; N, 4.7%); $\nu_{max.}$ 1 635 cm^{-1} (C=O).

Birch Reduction of 6-Methoxyindoline (9).—A solution of the indoline (9) (8.1 g) in dry tetrahydrofuran (20 ml) was added to liquid ammonia (400 ml). Lithium (3.0 g) was added to the resulting solution in small pieces with stirring over 10 min. After stirring for 10 min absolute methanol (40 ml) was added dropwise over 20 min. When the blue colour had disappeared the ammonia was allowed to evaporate overnight and the organic solvent was removed *in vacuo*. After addition of ice-cold water, the residue was extracted with ether, and the extract was dried (K_2CO_3) and evaporated to give a pale yellow oil. Distillation gave *3,3a,4,5-tetrahydro-6-methoxy-2H-indole* (18) (7.6 g, 92%), b.p. 76—77° at 1 mmHg, as an oil (Found: M^+, 151.0973. $C_9H_{13}NO$ requires M, 151.0997); $\lambda_{max.}$ 242.5 nm (log ε 4.27); $\nu_{max.}$ (neat) 1 625 cm^{-1} (C=N and C=C); δ 3.66 (3 H, s, OMe) and 5.62 (1 H, s, olefinic); for ^{13}C n.m.r. data see Table.

1,2,3,3a,4,5-Hexahydroindol-6-one (19).—A solution of the imino-enol ether (18) (1.74 g) in 2N-hydrochloric acid (50 ml) was heated under reflux for 1 h, cooled, and basified with potassium carbonate; the precipitate was collected by filtration. Recrystallisation from benzene–hexane gave the *enamino-ketone* (19) (1.29 g, 81.7%) as prisms, m.p. 143—144° (Found: C, 69.9; H, 8.15; N, 10.05. $C_8H_{11}NO$ requires C, 70.05; H, 8.1; N, 10.2%); $\lambda_{max.}$ 286.5 nm (log ε 4.52); $\nu_{max.}$ 3 440 (NH), 1 620sh (C=O), and 1 580 cm^{-1} (C=C); δ 5.17 (1 H, s, olefinic). The aqueous filtrate was extracted with chloroform; the extract was washed with water, dried (K_2CO_3), and evaporated to leave starting material (42 mg).

Conversion of the Enamino-ketone (19) *into the Imino-enol Ether* (18) *with Methyl Iodide*.—A solution of the enaminoketone (19) (500 mg) and methyl iodide (10 ml) in dry chloroform (20 ml) was heated under reflux for 45 h. Evaporation left a gum which was dissolved in chloroform. The solution was shaken repeatedly with aqueous 10% potassium carbonate, washed with saturated aqueous sodium chloride, dried (K_2CO_3), and evaporated to leave an oil, which was chromatographed on neutral alumina. Elution with chloroform gave 3,3a,4,5-tetrahydro-6-methoxy-2*H*-indole (18) (170 mg) as a pale yellow oil, identical (t.l.c. and i.r. and n.m.r. spectroscopy) with the sample obtained by Birch reduction of 6-methoxyindoline (9).

N-*Benzoyl-1,2,3,3a,4,5-hexahydroindol-6-one* (20).—A solution of benzoyl chloride (0.52 g) in dry ether (10 ml) was added simultaneously with 0.4N-sodium hydroxide (10 ml) to a solution of the imino-enol ether (19) (0.50 g) in ether (20 ml) with stirring over 30 min in an ice-bath. The ethereal layer was separated, washed with 5% hydrochloric acid then with water, and dried ($MgSO_4$). Evaporation left a pale yellow solid, which was recrystallised from ethyl acetate to give the *enamido-ketone* (20) (0.33 g, 41%) as plates, m.p. 186—187° (Found: C, 74.35; H, 6.2; N, 5.45. $C_{15}H_{15}NO_2$ requires C, 74.65; H, 6.25; N, 5.8%); $\lambda_{max.}$ 231 (log ε 3.80) and 292 nm (4.19); $\nu_{max.}$ 1 670br, 1 642, and 1 602 cm^{-1}; δ 6.37 (1 H, d, *J* 2 Hz, olefinic) and 7.51 (5 H, s, aromatic); *m/e* 241 (M^+), 231, 185, 105 (base), and 77.

1,2,3,3a,4,5-Hexahydro-N-(3,4-methylenedioxybenzoyl)indol-6-one (21).—A solution of 3,4-methylenedioxybenzoyl chloride (4.4 g) in dry benzene (60 ml) was added simultaneously with 0.4N-sodium hydroxide (60 ml) to a solution of the imino-enol ether (18) (3.0 g) in ether (100 ml) with stirring over 30 min in an ice-bath. The product, worked up as described for compound (20), crystallised from chloroform–hexane as *plates* (2.32 g, 41%), m.p. 202—203° (Found: C, 67.3; H, 5.25; N, 4.8. $C_{16}H_{15}NO_4$ requires C, 67.35; H, 5.3; N, 4.9%); $\lambda_{max.}$ 235 (log ε 4.08) and 300 nm (4.26); $\nu_{max.}$ 1 667, 1 642, and 1 606 cm^{-1}; δ 6.06 (2 H, s, OCH_2O), 6.26 (1 H, d, *J* 2 Hz, olefinic), 6.85 (1 H, d, *J* 8 Hz, 5′-H), 7.30 (1 H, s, 2′-H), and 7.16 (1 H, dd, $J_{5',6'}$ 8, $J_{2',6'}$ 2 Hz, 6′-H); *m/e* 285 (M^+), 257, 229, 149 (base), and 121.

Irradiation of the Enamido-ketones (20) *and* (21).—(*a*) A solution of the enamido-ketone (20) (300 mg) in methylene chloride (200 ml) was irradiated with a 6 W low pressure mercury lamp (Ushio) at room temperature for 12 h. The solvent was removed and the residue was chromatographed on silica gel with benzene–ethyl acetate (95 : 5) as eluant. The resulting solid was recrystallised from ethanol to give *3,3a,4,5-tetrahydropyrrolo*[3,2,1-de]*phenanthridine-1,7(2H)-dione* (22) (205 mg, 69%) as needles, m.p. 217—218° (Found: C, 75.4; H, 5.55; N, 5.85. $C_{15}H_{13}NO_2$ requires C, 75.3; H, 5.5; N, 5.85%); $\lambda_{max.}$ 221.5 (log ε 4.38), 245 infl(4.16), 296.5 (4.06), 310.5 (3.96), 323.5 (4.00), and 338 nm (3.87); $\nu_{max.}$ 1 645, 1 625sh, and 1 605sh cm^{-1}; δ 8.40 (1 H, dd, *J* 8 and 2 Hz, 8-H) and 9.22 (1 H, dd, *J* 8 and 2 Hz, 11-H); *m/e* 239 (M^+), 211 (base), 210, and 182.

(*b*) A solution of the enamido-ketone (21) (500 mg) in tetrahydrofuran (300 ml) was irradiated as in (*a*). The solvent was removed and the resulting pale yellow solid was recrystallised from ethanol to give *3,3a,4,5-tetrahydro-9,10-methylenedioxypyrrolo*[3,2,1-de]*phenanthridine-1,7(2H)-dione* (23) (345 mg, 70%) as needles, m.p. 252—253° (Found: C, 67.6; H, 4.6; N, 5.0. $C_{16}H_{13}NO_4$ requires C, 67.85; H, 4.65; N, 4.95%); $\lambda_{max.}$ 247 (log ε 4.51), 265 (4.47), 303 (3.87), 330 (4.00), and 344.5 nm (4.00); $\nu_{max.}$ 1 645, 1 620, and 1 592 cm^{-1}; δ 6.10 (2 H, s, OCH_2O), 7.67 (1 H, s, 8-H), and 8.62 (1 H, s, 11-H); *m/e* 283 (M^+, base), 255, and 227.

(*c*) A solution of the enamido-ketone (21) (1.40 g) in tetrahydrofuran (200 ml) was irradiated with a 100 W high pressure mercury lamp (Ushio) at room temperature for 1 h. T.l.c. showed that no starting material remained in the solution. The solvent was removed to leave a pale yellow solid, which was recrystallised from ethanol to yield the photoproduct (23) (0.73 g). The mother liquor was evaporated and the residue was chromatographed on silica gel. Elution with benzene–ethyl acetate (95 : 5) gave an additional 0.24 g of the product (23); total yield 0.97 g (70%).

1,2,3,3a,4,5-Hexahydro-9,10-methylenedioxypyrrolo[3,2,1-de]*phenanthridin-7-one* (25).—A solution of the oxo-lactam (23) (300 mg) in acetic acid (20 ml) containing Adams catalyst (30 mg) was hydrogenated at 1 atm until absorption ceased. Evaporation of the filtered solution gave the *isoquinolin-1-one derivative* (25) (305 mg, 92%) as plates (from acetone–hexane), m.p. 166—168° (Found: C, 71.25; H, 5.65; N, 5.0. $C_{16}H_{15}NO_3$ requires C, 71.35; H, 5.6; N, 5.2%); $\lambda_{max.}$ 228 (log ε 4.28), 250.5 (4.37), 267.5 (4.40), 287 (4.13), 298.5 (4.14), 323infl (3.86), 336.5 (3.96), and 350.5 nm (3.86); $\nu_{max.}$ 1 675m (C=O) and 1 600s cm^{-1} (ring); δ 6.07 (2 H, s, OCH_2O),

6.87 (1 H, s, 11-H), and 7.83 (1 H, s, 8-H); *m/e* 269 (M^+, base) and 241.

(±)-β-*Anhydrodihydrocaranine*[(±)-1,12b-*Didehydrolycoran*] (3).—A solution of the oxo-lactam (23) (140 mg) in dry tetrahydrofuran (50 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (60 mg) in the same solvent (50 ml) at ice-bath temperature. The mixture was heated under reflux for 15 h, decomposed with moist tetrahydrofuran, then with ice–water, and filtered. The filtrate was evaporated and the residue was extracted with benzene. The extract was washed with water, dried (K_2CO_3), and evaporated to leave a red-brown oil which was chromatographed on alumina. Elution with benzene gave a pale yellow solid which was recrystallised from hexane to give (±)-α-*anhydrodihydrocaranine* (3) (30 mg, 32%) as needles, m.p. 106—107° (Found: C, 75.4; H, 6.75; N, 5.45. $C_{16}H_{17}NO_2$ requires C, 75.25; H, 6.7; N, 5.5%); $\lambda_{max.}$ 263 (log ε 4.11) and 310 nm (3.86); $\nu_{max.}$ 1 645 cm^{-1} (styrene C=C); δ 3.20 (1 H, t, $J_{1,12c} = J_{3a,12c} = 7.5$ Hz, 12c-H), 3.49 and 4.08 (2 H, AB-type q, J 14.5 Hz, 7-H_2), 5.92 (2 H, s, OCH_2O), 6.24 (1 H, m, 1-H), 6.53 (1 H, s, 8-H), and 7.06 (1 H, s, 12-H); *m/e* 255 (M^+, base) and 227.

(±)-γ-*Lycoran*[(±)-12bα-*Lycoran*] (5).—α-Anhydrodihydrocaranine (3) (40 mg) was hydrogenated at 1 atm over Adams catalyst (10 mg) in acetic acid (4 ml) at room temperature. Evaporation of the filtered solution left a residue which was basified with aqueous potassium carbonate and extracted with benzene. The extract was filtered, dried (K_2CO_3), and evaporated to leave a syrup which was chromatographed on alumina (4.0 g). Elution with benzene gave (±)-γ-*lycoran* (5) (19 mg, 47%) as prisms (from hexane), m.p. 102—104° (lit.,[4,5a,c] 101—102°; lit.,[5b] 102—104°), identical (i.r. spectrum in CS_2) with an authentic sample, δ 3.21 and 4.01 (2 H, AB-type q, J 14.5 Hz, 7-H_2), 5.88 (2 H, s, OCH_2O), 6.49 (1 H, s, 8-H), and 6.61 (1 H, s, 12-H).

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