[Chem. Pharm. Bull. 26(11)3330—3337(1978)]

UDC 547.833.9.04 : 547.655.6.04

Heterocycles. VI.[1] An Approach to Corynoline Analogues

Masayuki Onda, Yoshihiro Harigaya, and Junya Horie

School of Pharmaceutical Sciences, Kitasato University[2]

(Received March 17, 1978)

The 2-methyl ketone (**2a, b**), which are derived from the ketones (**1a, b**), afford the *cis*-imines (**7a, b**) and *trans*-imines (**8a, b**) by the Leuckart and Bischler-Napieralski reactions. Their methiodides (**9a, b** and **10b**) are converted into the *cis*-lactams (**15a, b**) and *trans*-lactam (**17b**) *via* oxidation of the pseudo cyanides (**14a, b** and **16b**). Bromination and successive dehydrobromination of **2a** give the enone (**20**) which affords the *cis*-imine (**23**) and *trans*-imine (**24**) by the same procedure as above. The *cis*-methiodide (**25**) of **23** is reduced to give the *cis*-amine (**26**). The *cis*-lactams (**15a, b**) and *cis*-amine (**26**) can be connected with the synthetic methods of corynoline analogues, which were already known.

Keywords——benzo[*c*]phenanthridines; Leuckart reaction; Bischler-Napieralski reaction; potassium ferricyanide oxidation; NMR

The synthetic method of benzo[*c*]phenanthridines, which started from the condensation of aromatic aldehydes and acetophenones, has been established as a useful one.[3] We have investigated its application to the syntheses of corynoline analogues. Since the syntheses of corynoline and its analogues have been achieved,[4] the objective of the present work is to prepare the key intermediates for the syntheses of these alkaloids. We now report this attempt in detail, which has been described in our preliminary communication,[1] together with some further results obtained.

The ketones (**1a, b**) were smoothly prepared in several steps from piperonal and acetophenones.[3] Methylations of **1a** and **1b** with methyl iodide in the presence of sodium hydride gave the 2-methyl ketones (**2a, b**) and 2-methoxy ketones (**3a, b**) in 74, 70, 13 and 5% yields, respectively. Their nuclear magnetic resonance (NMR) spectra show the signals for the newly introduced Me and OMe groups at δ 1.50—1.48 and 3.30—3.29, respectively. Since the base-catalyzed autoxidation of **1a** afforded the 2-hydroxy ketone (**4**) which was then methylated to give **3a**, these facts are considered to explain the formation pathway of **3a** from **1a** during the above methylation. The Leuckart reaction of **2a** and **2b** provided a mixture of the *cis*[5]-amides (**5a, b**) and *trans*[5]-amides (**6a, b**) which were purified to afford the amides (**5a, b** and **6a, b**) in 20, 12, 16 and 14% yields, respectively. Their structures are assigned on the basis of the compounds obtained by the following reaction. The Bischler-Napieralski reaction of **5a, 5b, 6a** and **6b** smoothly gave the *cis*-imines (**7a, b**) and *trans*-imines (**8a, b**). Their structures are examined by the NMR spectroscopy. From the allylic coupling constants ($J_{4b,6}$ 3—3.5 Hz), the 4b-H's in all compounds are considered to be axial to the

1) M. Onda, Y. Harigaya, and J. Horie, *Heterocycles*, **8**, 89 (1977).
2) Location: *Minato-ku, Tokyo 108, Japan.*
3) T. Richardson, R. Robinson, and E. Seijo, *J. Chem. Soc.*, **1937**, 835; K.W. Gopinath, T.R. Govindachari, K. Nagarajan, and N. Viswanathan, *ibid.*, **1957**, 4760; H.R. Arthur and Y.L. Ng, *ibid.*, **1959**, 4010; K.W. Gopinath, T.R. Govindachari, P.C. Parthasarathy, and N. Viswanathan, *ibid.*, **1959**, 4012; K.-Y. Zee-Cheng, and C.C. Cheng, *J. Heterocycl. Chem.*, **10**, 85 (1973).
4) *a*) M. Onda, K. Yuasa, and J. Okada, *Chem. Pharm. Bull.* (Tokyo), **22**, 2365 (1974); *b*) I. Ninomiya, O. Yamamoto, and T. Naito, *Heterocycles*, **4**, 743 (1976); *c*) G. Nonaka and I. Nishioka, *Chem. Pharm. Bull.* (Tokyo), **23**, 521 (1975); I. Ninomiya, O. Yamamoto, and T. Naito, *Heterocycles*, **5**, 67 (1976); *idem*, *J. Chem. Soc., Chem. Commun.*, **1976**, 437.
5) This nomenclature is referred to the steric relationship between the 1-H and 2-Me group.

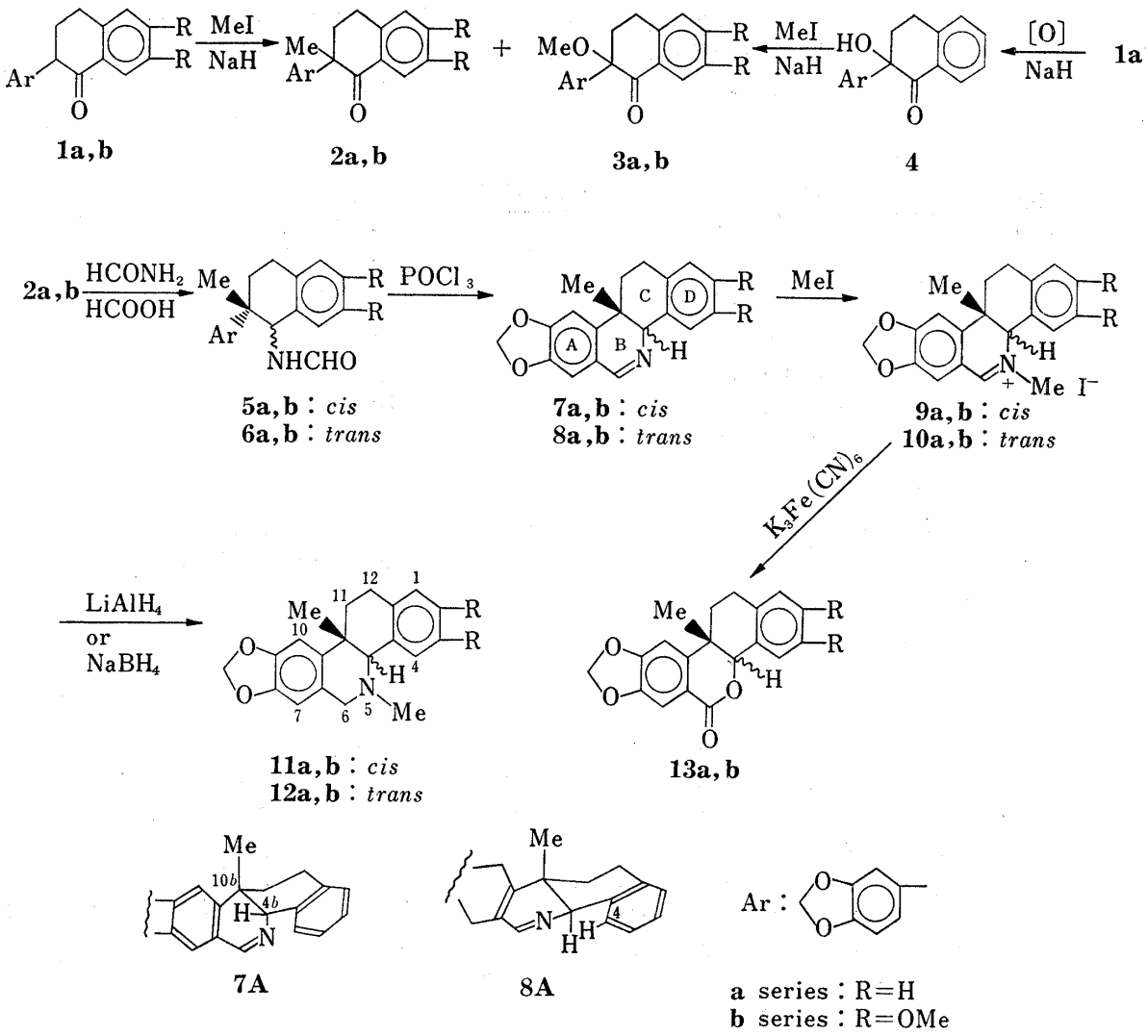

Chart 1

B ring.[6] As can be seen from the *cis* conformer (**7A**), the 4b-H and 10b-Me group lie in the deshielding zones of the D and A rings, respectively. As a result, downfield shifts of their chemical shifts are predictable. From examination of the stereostructure (**8A**), downfield shifts of the 4-H and 10-H are anticipated for **8a** and **8b** owing to interaction of the nitrogen lone pair[7] and 11-H. Their NMR data are as follows: $\Delta\delta_a^{4\text{-H}}=-0.59$ ppm,[8] $\Delta\delta_a^{4b\text{-H}}=+0.27$ ppm, $\Delta\delta_a^{10\text{-H}}=-0.17$ ppm, $\Delta\delta_a^{10b\text{-Me}}=+0.45$ ppm; $\Delta\delta_b^{4\text{-H}}=-0.43$ ppm, $\Delta\delta_b^{4b\text{-H}}=+0.30$ ppm, $\Delta\delta_b^{10\text{-H}}=-0.13$ ppm, $\Delta\delta_b^{10b\text{-Me}}=+0.42$ ppm. From the above consideration and their NMR data, the *cis* isomer for **7a** and **7b** and *trans* one for **8a** and **8b** can be assigned. Their methiodides (**9a**, **b** and **10a**, **b**) were reduced with lithium aluminium hydride or sodium borohydride to give the *cis*-amines (**11a**, **b**) and *trans*-amines (**12a**, **b**). The NMR spectra of **11a** and **11b** are very resembled to that of 10b-methyl-*cis*-4b,5,6,10b,11,12-hexahydrochelerythrine,[9] supporting their structures. However, the NMR signals for the 4-H,

6) B.R. Lowry and A.C. Huitric, *J. Org. Chem.*, **37**, 2697 (1972); M. Barfield, R.J. Spear, and S. Sternhell, *Chem. Rev.*, **76**, 593 (1976).
7) T.A. Crabb, "Annual Reports on NMR Spectroscopy," Vol 6A, ed. by E.F. Mooney, Academic Press, London, **1975**, p. 350.
8) $\Delta\delta_a^{4\text{-H}}=\delta_{7a}^{4\text{-H}}(7.51)-\delta_{8a}^{4\text{-H}}(8.10)$.
9) M. Onda, K. Yuasa, J. Okada, K. Kataoka (née Yonezawa), and K. Abe, *Chem. Pharm. Bull.* (Tokyo), **21**, 1333 (1973).

4b-H, 5-Me and 6-H_2 in **12a** and **12b** appear at lower fields compared with those in **11a** and **11b**. This would be ascribed to deformation of the half-chair form of the B rings in the former two compounds caused by interaction between the 5-Me group and 4-H or 10b-Me group.[10]

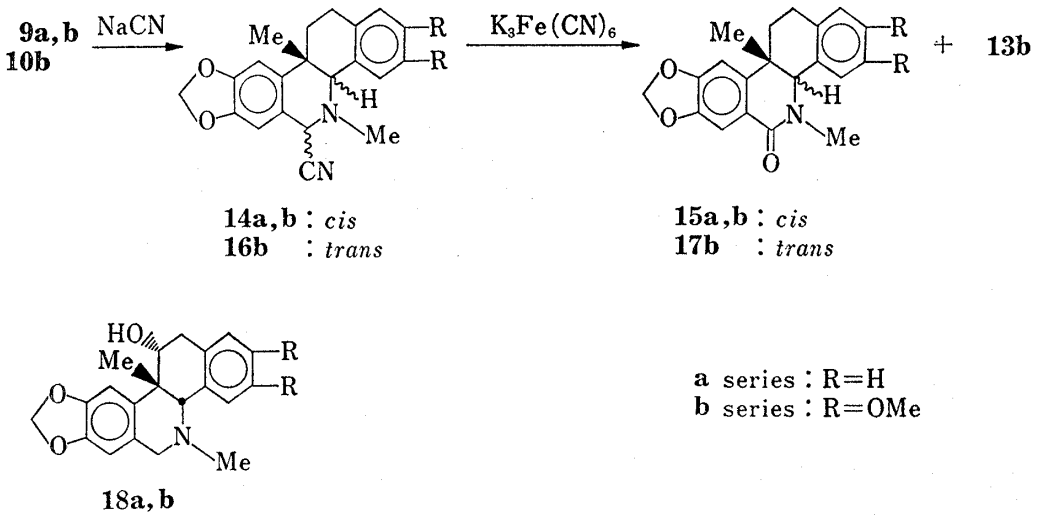

Chart 2

Oxidation of **9a** with potassium ferricyanide in the presence of potassium hydroxide unexpectedly gave the lactone (**13a**) in 65% yield. The presence of the lactone group in **13a** is proved by its infrared (IR) spectrum showing the carbonyl band at 1715 cm^{-1}. After conversions of **9a** and **9b** into the pseudo cyanides (**14a, b**), their oxidations with potassium ferricyanide afforded the *cis*-lactams (**15a, b**). By the same procedure **10b** gave the *trans*-lactam (**17b**) and lactone (**13b**) in an approximate ratio of 2:1. The NMR spectra of **15a**, **15b** and **17b** can be reasonably assigned by analogy with those of the related compounds.[4,11]

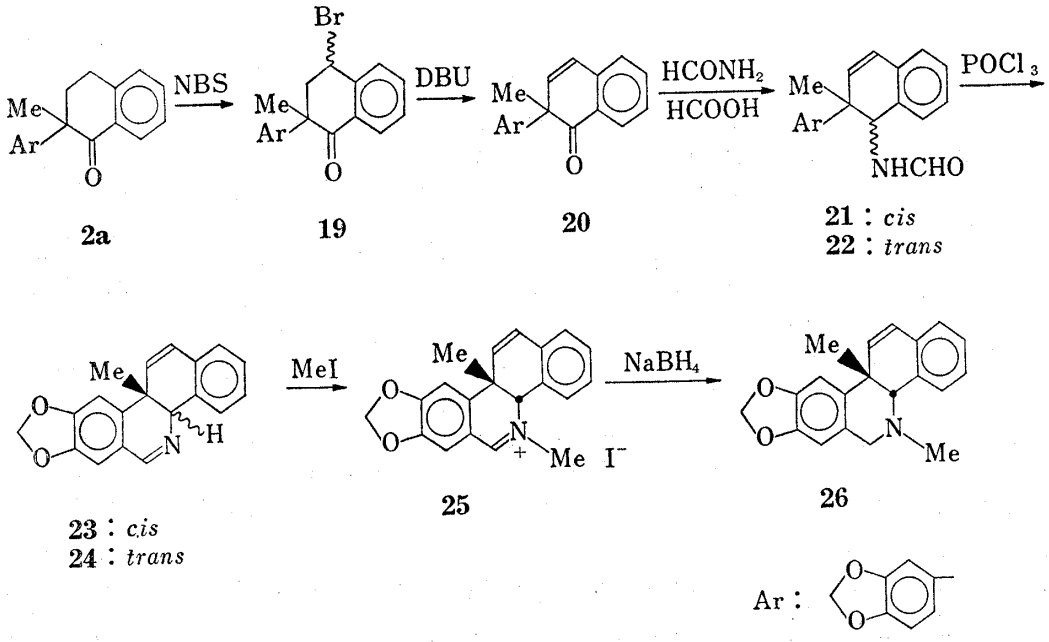

Chart 3

10) I. Ninomiya, T. Naito, T. Kiguchi, and T. Mori, *J. Chem. Soc., Perkin I*, 1973, 1696.
11) I. Ninomiya, T. Naito, H. Ishii, T. Ishida, M. Ueda, and K. Harada, *J. Chem. Soc., Perkin I*, 1975, 762.

The *cis*-lactam (**15a**) was not converted into **13a** under the oxidation conditions as above. Up to now, the formation pathways of **13a** and **13b** from **9a** and **10b** have not been able to elucidate.

The synthetic pathways from **15a** and **15b** to the corynoline analogues (**18a, b**) are considered to connect with the known one.[4a,b] The synthesis of the 4b-*epi* analogue can also be expected from **17b**.

Bromination of **2a** (→**19**) with N-bromosuccinimide (NBS) followed by dehydrobromination with 1,5-diazabicyclo[5.4.0]undecene-5 (DBU) afforded the enone (**20**) in 57% yield. Its NMR spectrum shows two doublets (J 10 Hz) at δ 6.70 and 6.22, showing the presence of the double bond. The Leuckart reaction of **20** gave the *cis*[5]-amide (**21**) and *trans*[5]-amide (**22**) in 52 and 30% yields, respectively. Their structures are assigned on the basis of the compounds obtained by the following reaction. The amides (**21** and **22**) afforded the *cis*-imine (**23**) and *trans*-imine (**24**) in 58 and 43% yields. From examination of the Dreiding model and a similar consideration to that in the cases of **7a, 7b, 8a** and **8b**, downfield shifts of the 4b-H and 10b-Me group in **23** and the 4-H in **24** are predicted in their NMR spectra. Further, since the 11-H in **23** lies in the shielding zone of the A ring, this proton must be shielded.[12] Owing to steric interaction, the 10-H and 11-H in **24** are expected to shift to lower fields. The NMR data of **23** and **24** are in accord with the above consideration as follows: $\Delta\delta^{4\text{-H}}=-0.75$ ppm,[13] $\Delta\delta^{4b\text{-H}}=+0.17$ ppm, $\Delta\delta^{10\text{-H}}=-0.35$ ppm, $\Delta\delta^{10b\text{-Me}}=+0.55$ ppm, $\Delta\delta^{11\text{-H}}=-0.77$ ppm. $J_{4b,6}$ 3 Hz for **23** and **24**. Thus, the stereostructures of **23** and **24** have been decided to be *cis* and *trans*, respectively. The *cis*-methiodide (**25**), which was obtained from **23** in 81% yield, was reduced with sodium borohydride to give the *cis*-amine (**26**) in 84% yield. Its NMR signals observed can be reasonably assigned, supporting the structure of **26**.

The *cis*-amine (**26**) can also be connected with the synthesis of **18a**.[4c]

Experimental

Melting points were determined on a micro hot-stage and are not corrected. IR spectra were recorded on a JASCO IR-G. NMR spectra were taken on a Varian T-60 (60 MHz) and a JEOL JNM PS-100 (100 MHz) in a deuterochloroform solution unless otherwise stated. Mass spectra (MS) were measured with a JEOL JMS-OIS.

2-(3′,4′-Methylenedioxyphenyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (1a) and 6,7-Dimethoxy-2-(3′,4′-methylenedioxyphenyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (1b)——These compounds were prepared by the procedures described in the literature.[3]

The Ketone (**1a**): Colorless needles of mp 135—136.5° (from MeOH). IR ν_{max}^{KBr} cm^{-1}: 1672 (C=O). *Anal.* Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.31. Found: C, 76.47; H, 5.29.

The Ketone (**1b**): Colorless prisms of mp 172—174° (from MeOH). IR ν_{max}^{KBr} cm^{-1}: 1662 (C=O). *Anal.* Calcd. for $C_{19}H_{18}O_5$: C, 69.92; H, 5.57. Found: C, 70.07; H, 5.65.

2-Methyl-2-(3′,4′-methylenedioxyphenyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (2a) and 2-Methoxy-2-(3′,4′-methylenedioxyphenyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (3a)——A mixture of **1a** (1.0 g), methyl iodide (2.7 g) and 50% NaH-mineral oil (210 mg) in dry benzene (20 ml) was refluxed for 8 hr under N_2. After each 3 hr, methyl iodide (2.7 g) was added. The reaction mixture was acidified with acetic acid and the benzene layer was washed with H_2O. The work-up afforded an oil (1.1 g) which was purified by column chromatography (Al_2O_3, grade III; 90 g). The fraction eluted with benzene–hexane (1: 1, v/v) gave **2a** (777 mg, 74%) as colorless prisms of mp 104.5—105° (from EtOH). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1681 (C=O). NMR (60 MHz) δ: 8.14 (1H, dd, J 8 and 2 Hz, 8-H), 7.47—7.01 (3H, m, 5-, 6- and 7-H), 6.75 (1H, s, 2′-H), 6.67 (2H, s, 5′- and 6′-H), 5.89 (2H, s, OCH_2O), 2.97—2.69 (2H, m, 4-H_2), 2.57—2.01 (2H, m, 3-H_2), 1.50 (3H, s, 2-Me). *Anal.* Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.96; H, 5.72. MS *m/e*: M$^+$, 280.112 (M, 280.110). The fraction eluted with benzene–hexane (3: 1, v/v) gave **3a** (134 mg, 13%) as an oil. IR ν_{max}^{film} cm^{-1}: 1692 (C=O). NMR (60 MHz) δ: 8.10 (1H, dd, J 7 and 2 Hz, 8-H), 7.48—7.05 (3H, m, 5-, 6- and 7-H), 6.86 (1H, d, J 1 Hz, 2′-H), 6.73 (2H, br s, 5′- and 6′-H), 5.92 (2H, s, OCH_2O), 3.30 (3H, s, OMe), 3.08—2.70 (2H, m, 4-H_2), 2.63—2.30 (2H, m, 3-H_2). MS *m/e*: M$^+$, 296.103. Calcd. for $C_{18}H_{16}O_4$: M, 296.105.

12) The assignments for the chemical shifts of the 11-H and 12-H in the keto amide (**11**), the carbinol amide (**14**) and lactam (**15**) described in the literature[4a] are revised herein to exchange.

13) $\Delta\delta^{4\text{-H}}=\delta_{23}^{4\text{-H}}(7.39)-\delta_{24}^{4\text{-H}}(8.14)$.

6,7-Dimethoxy-2-methyl-2-(3′,4′-methylenedioxyphenyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (2b) and 2,6,7-Trimethoxy-2-(3′,4′-methylenedioxyphenyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (3b)——A mixture of **1b** (1.0 g), methyl iodide (5 ml), 50% NaH-mineral oil (166 mg) in dry toluene (25 ml) was treated by the above procedure to give **2b** (748 mg, 70%) and **3b** (55 mg, 5%).

The 2-Methyl Ketone (**2b**): Colorless prisms of mp 148—150.5° (from EtOH). IR ν_{max}^{KBr} cm^{-1}: 1653 (C=O). NMR (60 MHz) δ: 7.61 (1H, s, 8-H), 6.74 (1H, s, 2′-H), 6.67 (2H, s, 5′- and 6′-H), 6.53 (1H, s, 5-H), 5.89 (2H, s, OCH_2O), 3.93 (3H, s, OMe), 3.88 (3H, s, OMe), 2.94—2.63 (2H, m, 4-H_2), 2.55—2.06 (2H, m, 3-H_2), 1.48 (3H, s, 2-Me). *Anal.* Calcd. for $C_{20}H_{20}O_5$: C, 70.56; H, 5.93. Found: C, 70.35; H, 5.95.

The 2-Methoxy Ketone (**3b**): Colorless prisms of mp 139.5—141° (from EtOH). IR ν_{max}^{KBr} cm^{-1}: 1675 (C=O). NMR (100 MHz) δ: 7.59 (1H, s, 8-H), 6.86 (1H, s, 2′-H), 6.72 (2H, s, 5′- and 6′-H), 6.57 (1H, s, 5-H), 5.92 (2H, s, OCH_2O), 3.92 (3H, s, OMe), 3.89 (3H, s, OMe), 3.29 (3H, s, 2-OMe), 3.09—2.68 (2H, m, 4-H_2), 2.59—2.32 (2H, m, 3-H_2). MS *m/e*: M$^+$, 356.124. Calcd. for $C_{20}H_{20}O_6$: M, 356.126.

2-Hydroxy-2-(3′,4′-methylenedioxyphenyl)-1-oxo-1,2,3,4-tetrahydronaphthalene (4)——1) To a solution of 50% NaH-mineral oil (200 mg) in dry methanol (7 ml) was added **1a** (620 mg) and the reaction mixture was refluxed for 9 hr with stirring. After cooling, the precipitate was collected and recrystallized from ethanol to give **4** (580 mg, 88%) as colorless prisms of mp 187—188.5°. IR ν_{max}^{KBr} cm^{-1}: 3520 (OH), 1686 (C=O). NMR (60 MHz) δ: 8.16 (1H, dd, *J* 7 and 2 Hz, 8-H), 7.55—7.12 (3H, m, 5-, 6- and 7-H), 6.90 (1H, d, *J* 2 Hz, 2′-H), 6.64 (2H, br s, 5′- and 6′-H), 5.91 (2H, s, OCH_2O), 4.11 (1H, s, 2-OH), 2.95—2.28 (4H, m, 3- and 4-H_2). *Anal.* Calcd. for $C_{17}H_{14}O_4$: C, 72.32; H, 5.01. Found: C, 72.12; H, 5.06.

2) The 2-hydroxy ketone (**4**) was recognized by TLC[14] (silica gel plates; benzene–ethyl acetate=10: 1, v/v) on refluxing a mixture of **1a** and 50% NaH-mineral oil in dry toluene.

The 2-Methoxy Ketone (3a) from 4——A mixture of **4** (580 mg), methyl iodide (2 ml) and 50% NaH-mineral oil (100 mg) in dry benzene (5 ml) was heated at 60° for 3 days. The work-up gave **3a** (504 mg, (83%) as an oil which was identified as **3a** by spectroscopy.

1-Formamido-2-methyl-2-(3′,4′-methylenedioxyphenyl)-1,2,3,4-tetrahydronaphthalenes (5a and 6a) and 1-Formamido-6,7-dimethoxy-2-methyl-2-(3′,4′-methylenedioxyphenyl)-1,2,3,4-tetrahydronaphthalenes (5b and 6b)——1) A stirring mixture of **2a** (2.0 g), formamide (10 ml), formic acid (0.5 ml) and $(NH_4)_2SO_4$ (250 mg) was heated at 180—190° for 21 hr. After cooling, the reaction mixture was diluted with H_2O and extracted with ethyl acetate. The residue obtained from the ethyl acetate layer was crystallized from ethanol to give **6a** (360 mg, 16%) as colorless crystals of mp 247—248°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3330 (NH), 1680 (NC=O). NMR (100 MHz) (DMSO-d_6)[15] δ: 8.25 (1H, dd, *J*10 and 2 Hz, NH), 8.09 (1H, d, *J* 2 Hz, CHO), 7.34—7.00 (4H, m, 5-, 6-, 7- and 8-H), 6.94 (1H, d, *J* 2 Hz, 2′-H), 6.79 (1H, dd, *J* 8 and 2 Hz, 6′-H), 6.71 (1H, d, *J* 8 Hz, 5′-H), 5.90 (2H, s, OCH_2O), 5.53 (1H, d, *J* 10 Hz, 1-H), 2.86—2.40 (2H, m, 4-H_2), 2.18—1.80 (2H, m, 3-H_2), 1.21 (3H, s, 2-Me). *Anal.* Calcd. for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.54; H, 6.18; N, 4.36. MS *m/e*: M$^+$, 309.139 (M, 309.137). The above filtrate gave an oil (*ca.* 1.7 g) whose column chromatography (Al_2O_3, grade III; 140 g) gave **5a** (450 mg, 20%) from the eluate with benzene–ethyl acetate (10: 1, v/v) as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420 (NH), 1685 (NC=O). NMR (60 MHz) δ: 7.89 (1H, d, *J* 2 Hz, CHO), 7.38—7.03 (4H, m, 5-, 6-, 7- and 8-H), 6.85 (1H, s, 2′-H), 6.72 (2H, s, 5′- and 6′-H), 5.90 (1H, dd, *J* 10.5 and 2 Hz, NH), 5.88 (2H, s, OCH_2O), 5.41 (1H, d, *J* 10.5 Hz, 1-H), 2.96—2.72 (2H, m, 4-H_2), 2.14—1.85 (2H, m, 3-H_2), 1.36 (3H, s, 2-Me). MS *m/e*: M$^+$, 309.138. Calcd. for $C_{19}H_{19}NO_3$: M, 309.137.

2) The *cis*-amide (**5b**) (13 mg, 12%) and *trans*-amide (**6b**) (15 mg, 14%) were obtained from **2b** (100 mg) by the above procedure.

The *cis*-Amide (**5b**): Colorless needles of mp 206.5—208° (from benzene). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430 (NH), 1682 (NC=O). NMR (100 MHz) δ: 7.98 (1H, d, *J* 2 Hz, CHO), 6.88 (2H, s, 8- and 2′-H), 6.76 (2H, s, 5′- and 6′-H), 6.58 (1H, s, 5-H), 5.92 (2H, s, OCH_2O), 5.53 (1H, br s, NH), 5.43 (1H, s, 1-H), 3.84 (6H, s, 2×OMe), 2.91—2.73 (2H, m, 4-H_2), 2.23—1.81 (2H, m, 3-H_2), 1.34 (3H, s, 2-Me). *Anal.* Calcd. for $C_{21}H_{23}NO_5$: C, 68.27; H, 6.29; N, 3.79. Found: C, 69.07; H, 6.24; N, 3.38. MS *m/e*: M$^+$, 369.155 (M, 369.158).

The *trans*-Amide (**6b**): A colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430 (NH), 1688 (NC=O). NMR (100 MHz) δ: 8.27 (1H, s, CHO), 6.87 (1H, s, 2′-H), 6.76 (3H, s, 8-, 5′- and 6′-H), 6.46 (1H, s, 5-H), 5.88 (2H, s, OCH_2O), 5.68 (2H, br s, 1-H and NH), 3.83 (6H, s, 2×OMe), 2.89—2.43 (2H, m, 4-H_2), 2.35—1.70 (2H, m, 3-H_2), 1.30 (3H, s, 2-Me). MS *m/e*: M$^+$, 369.155. Calcd. for $C_{21}H_{23}NO_5$: M, 369.158.

10b-Methyl-8,9-methylenedioxy-4b,10b,11,12-tetrahydrobenzo[*c*]phenanthridines (7a and 8a) and 2,3-Dimethoxy-10b-methyl-8,9-methylenedioxy-4b,10b,11,12-tetrahydrobenzo[*c*]phenanthridines (7b and 8b)——1) A solution of **5a** (277 mg) and $POCl_3$ (0.6 ml) in dry toluene (6 ml) was stirred at room temperature for 2 hr. The reaction mixture was made alkaline with aq. NaOH solution and extracted with benzene, giving an oil (259 mg). Its preparative TLC (silica gel plates; benzene–ethyl acetate=5: 1, v/v) and crystallization from ethanol gave **7a** (193 mg, 74%) as colorless prisms of mp 164—165°. IR ν_{max}^{KBr} cm^{-1}: 1637 (C=N). NMR (60 MHz) δ: 8.17 (1H, d, *J* 3 Hz, 6-H), 7.52 (1H, dd, *J* 8 and 3 Hz, 4-H), 7.28—6.95 (3H, m, 1-,

14) Thin-layer chromatography.
15) Dimethyl sulfoxide-d_6.

2- and 3-H), 6.90 (1H, s, 7-H), 6.70 (1H, s, 10-H), 5.96 (2H, s, OCH_2O), 4.56 (1H, d, *J* 3 Hz, 4b-H), 2.79 (2H, t, *J* 7 Hz, 12-H_2), 2.34—1.50 (2H, m, 11-H_2), 1.30 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.03; H, 5.89; N, 4.71. MS *m/e*: M^+, 291.125 (M, 291.126).

The *cis*-Methiodide (**9a**): Yellow needles of mp 227—228° (from EtOH). *Anal.* Calcd. for $C_{20}H_{20}INO_2 \cdot 1/2H_2O$: C, 54.31; H, 4.79; N, 3.18. Found: C, 54.09; H, 4.58; N, 3.09.

2) The *trans*-imine (**8a**) (171 mg, 61%) was obtained from **6a** (290 mg) as colorless prisms of mp 157—158.5° (from EtOH) by the above procedure. IR ν_{max}^{KBr} cm^{-1}: 1633 (C=N). NMR (60 MHz) δ: 8.42(1H,d, *J* 3 Hz, 6-H), 8.10 (1H, dd, *J* 8 and 3 Hz, 4-H), 7.45—7.07 (3H, m, 1-, 2- and 3-H), 6.91 (1H, s, 7-H), 6.87 (1H, s, 10-H), 6.00 (2H, s, OCH_2O), 4.29 (1H, d, *J* 3 Hz, 4b-H), 3.04 (2H, dd, *J* 10 and 4 Hz, 12-H_2), 2.56—1.82 (2H, m, 11-H_2), 0.85 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.31; H, 5.93; N, 4.71. MS *m/e*: M^+, 291.124 (M, 291.126).

The *trans*-Methiodide (**10a**): Yellow crystals of mp 173.5° (from EtOH). *Anal.* Calcd. for $C_{20}H_{20}INO_2 \cdot 1/5H_2O$: C, 54.98; H, 4.71; N, 3.21. Found: C, 55.11; H, 4.66; N, 3.40.

3) The *cis*-imine (**7b**) was obtained as a colorless oil in quantitative yield from **5b** (47 mg) by the above procedure. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640 (C=N). NMR (60 MHz) δ: 8.15 (1H, d, *J* 3 Hz, 6-H), 7.05 (1H, s, 4-H), 6.89 (1H, s, 7-H), 6.72 (1H, s, 10-H), 6.48 (1H, s, 1-H), 5.95 (2H, s, OCH_2O), 4.50 (1H, d, *J* 3 Hz, 4b-H), 3.91 (3H, s, OMe), 3.80 (3H, s, OMe), 2.71 (2H, t, *J* 7 Hz, 12-H_2), 2.36—1.50 (2H, m, 11-H_2), 1.28 (3H, s, 10b-Me). MS *m/e*: M^+, 351.147. Calcd. for $C_{21}H_{21}NO_4$: M, 351.147.

The *cis*-Methiodide (**9b**): Yellow crystals of mp 196.5—199° (from EtOH). *Anal.* Calcd. for $C_{22}H_{24}INO_4$: C, 53.55; H, 4.91; N, 2.84. Found: C, 53.35; H, 4.81; N, 2.83.

4) The *trans*-imine (**8b**) (23 mg, 59%) was obtained as light yellow crystals of mp 202—206° (from EtOH) from **6b** (41 mg) by the above procedure. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1632 (C=N). NMR (60 MHz) δ: 8.38 (1H, d, *J* 3.5 Hz, 6-H), 7.62 (1H, s, 4-H), 6.88 (1H, s, 7-H), 6.85 (1H, s, 10-H), 6.64 (1H, s, 1-H), 5.98 (2H, s, OCH_2O), 4.20 (1H, d, *J* 3.5 Hz, 4b-H), 3.95 (3H, s, OMe), 3.87 (3H, s, OMe), 2.97 (2H, dd, *J* 10 and 4 Hz, 12-H_2), 2.53—1.83 (2H, m, 11-H_2), 0.86 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{21}H_{21}NO_4$: C, 71.77; H, 6.04; N, 3.99. Found: C, 71.78; H, 6.00; N, 3.79.

The *trans*-Methiodide (**10b**): Yellow prisms of mp 184.5—188° (from EtOH). *Anal.* Calcd. for $C_{22}H_{24}INO_4$: C, 53.55; H, 4.91; N, 2.84. Found: C, 53.48; H, 4.84; N, 3.02.

5,10b-Dimethyl-8,9-methylenedioxy-4b,5,6,10b,11,12-hexahydrobenzo[*c*]phenanthridines (11a and 12a) and 2,3-Dimethoxy-5,10b-dimethyl-8,9-methylenedioxy-4b,5,6,10b,11,12-hexahydrobenzo[*c*]phenanthridines (11b and 12b)——1) To a stirring solution of $LiAlH_4$ (60 mg) in dry ether (10 ml) was added **9a** (100 mg) and stirring was continued at room temperature for 1 hr. After addition of H_2O, the ether layer was separated. The work-up gave **11a** (65 mg, 90%) as colorless prisms of mp 149—150° (from EtOH). NMR (60 MHz) δ: 7.30—7.07 (4H, m, 1-, 2-, 3- and 4-H), 6.83 (1H, s, 10-H), 6.49 (1H, s, 7-H), 5.91 (2H, s, OCH_2O), 3.78 (1H, d, *J* 15.5 Hz, 6-H), 3.58 (1H, d, *J* 15.5 Hz, 6-H), 3.19 (1H, s, 4b-H), 2.96—2.71 (2H, m, 12-H_2), 2.22 (3H, s, 5-Me), 1.84—1.47 (2H, m, 11-H_2), 1.15 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.31; H, 6.87; N, 4.77. MS *m/e*: M^+, 307.157 (M, 307.157).

2) The *trans*-amine (**12a**) (21 mg, 75%) was obtained as colorless prisms of mp 107.5—108.5° (from EtOH) from **10a** (40 mg) by the above procedure. NMR (60 MHz) δ: 7.61 (1H, dd, *J* 8 and 3 Hz, 4-H), 7.33—7.10 (3H, m, 1-, 2- and 3-H), 6.89 (1H, s, 10-H), 6.58 (1H, s, 7-H), 5.93 (2H, s, OCH_2O), 4.29 (1H, d, *J* 17 Hz, 6-H), 4.11 (1H, s, 4b-H), 3.84 (1H, d, *J* 17 Hz, 6-H), 3.05—2.86 2H, m, 12-H_2), 2.52 (3H, s, 5-Me), 2.27—1.70 (2H, m, 11-H_2), 1.19 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.44; H, 6.92; N, 4.55. MS *m/e*: M^+, 307.157 (M, 307.157).

3) To a stirring solution of **9b** (12 mg) in methanol (2 ml) was added $NaBH_4$ (12 mg) and stirring was continued at room temperature for 5 min. After removal of the solvent *in vacuo*, the remaining residue was extracted with benzene to give **11b** (4 mg, 40%) as colorless prisms of mp 148.5—150° (from EtOH). NMR (100 MHz) δ: 6.81 (1H, s, 10-H), 6.74 (1H, s, 4-H), 6.60 (1H, s, 1-H), 6.47 (1H, s, 7-H), 5.88 (2H, s, OCH_2O), 3.85 (3H, s, OMe), 3.84 (3H, s, OMe), 3.78 (1H, d, *J* 16 Hz, 6-H), 3.61 (1H, d, *J* 16 Hz, 6-H), 3.12 (1H, s, 4b-H), 2.81—2.66 (2H, m, 12-H_2), 2.23 (3H, s, 5-Me), 1.80—1.54 (2H, m, 11-H_2), 1.13 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{22}H_{25}NO_4$: C, 71.90; H, 6.87; N, 3.81. Found: C, 71.68; H, 6.80; N, 3.72.

4) The *trans*-amine (**12b**) (5 mg, 54%) was obtained as colorless prisms of mp 179—182° (from EtOH) from **10b** (13 mg) by the above procedure. NMR (100 MHz) δ: 7.17 (1H, s, 4-H), 6.87 (1H, s, 10-H), 6.64 (1H, s, 1-H), 6.57 (1H, s, 7-H), 5.89 (2H, s, OCH_2O), 4.32 (1H, d, *J* 16 Hz, 6-H), 4.09 (1H, s, 4b-H), 3.89 (3H, s, OMe), 3.85 (3H, s, OMe), 3.81 (1H, d, *J* 16 Hz, 6-H), 3.02—2.84 (2H, m, 12-H_2), 2.48 (3H, s, 5-Me), 2.23—1.66 (2H, m, 11-H_2), 1.17 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{22}H_{25}NO_4$: C, 71.90; H, 6.87; N, 3.81. Found: C, 71.72; H, 6.81; N, 3.77.

10b-Methyl-8,9-methylenedioxy-5-oxa-6-oxo-4b,5,6,10b,11,12-hexahydrochrysene (13a)——To a solution of **9a** (100 mg) in ethanol (2.5 ml) were added a solution of $K_3Fe(CN)_6$ (160 mg) in H_2O (1.5 ml) and then 10% aq. KOH solution (0.65 ml). The reaction mixture was stirred at room temperature for 64 hr and diluted with H_2O to collect the precipitate (63 mg) which was recrystallized from ethanol to give **13a** (47 mg, 65%) as colorless needles of mp 220°. IR ν_{max}^{KBr} cm^{-1}: 1715 (OC=O). NMR (60 MHz) δ: 7.70 (1H, dd, *J* 8 and 4 Hz, 4-H), 7.57 (1H, s, 7-H), 7.37—7.11 (3H, m, 1-, 2- and 3-H), 6.85 (1H, s, 10-H), 6.05 (2H, s, OCH_2O),

5.34 (1H, s, 4b-H), 3.02 (2H, dd, J 8 and 2 Hz, 12-H_2), 2.59—1.75 (2H, m, 11-H_2), 1.12 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.77; H, 5.16. MS *m/e*: M^+, 308.109 (M, 308.105).

6-Cyano-5,10b-dimethyl-8,9-methylenedioxy-*cis*-4b,5,6,10b,11,12-hexahydrobenzo[*c*]phenanthridine (14a) and 6-Cyano-2,3-dimethoxy-5,10b-dimethyl-8,9-methylenedioxy-4b,5,6,10b,11,12-hexahydrobenzo[*c*]phenanthridines (14b and 16b)——1) To a mixture of **9a** (128 mg), benzene (2 ml) and methanol (2 ml) were added a solution of NaCN (37 mg) in H_2O (1 ml) and 15% aq. NaOH solution (0.3 ml). After stirring at room temperature for 4 hr, the precipitate was collected and recrystallized from ethanol to afford **14a** (86 mg, 87%) as colorless prisms of mp 172—175°. IR ν_{max}^{KBr} cm^{-1}: 2210 (C≡N). NMR (60 MHz) δ: 7.32—7.15 (4H, m, 1-, 2-, 3- and 4-H), 6.82 (1H, s, 10-H), 6.62 (1H, s, 7-H), 5.94 (2H, s, OCH_2O), 4.73 (1H, s, 6-H), 3.57 (1H, s, 4b-H), 2.96—2.74 (2H, m, 12-H_2), 2.62—2.02 (1H, m, 11-H), 2.21 (3H, s, 5-Me), 1.83—1.37 (1H, m, 11-H), 1.13 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{21}H_{20}N_2O_2$: C, 75.88; H, 6.06; N, 8.43. Found: C, 75.76; H, 6.07; N, 8.55. MS *m/e*: M^+, 332.157 (M, 332.153).

2) The *cis*-pseudo cyanide (**14b**) (146 mg, 85%) was obtained as colorless prisms of mp 164.5—168° (from EtOH) from **9b** (216 mg) by the above procedure. IR ν_{max}^{KBr} cm^{-1}: 2210 (C≡N). NMR (60 MHz) δ: 6.84 (1H, s, 10-H), 6.68 (1H, s, 4-H), 6.62 (2H, s, 1- and 7-H), 5.95 (2H, s, OCH_2O), 4.74 (1H, s, 6-H), 3.88 (6H, s, 2×OMe), 3.48 (1H, s, 4b-H), 2.93—2.59 (2H, m, 12-H_2), 2.51—2.06 (1H, m, 11-H), 2.26 (3H, s, 5-Me), 1.80—1.40 (1H, m, 11-H), 1.14 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{23}H_{24}N_2O_4$: C, 70.38; H, 6.18; N, 7.14. Found: C, 70.20; H, 6.21; N, 7.03.

3) The *trans*-pseudo cyanide (**16b**) (64 mg, 96%) was obtained as colorless prisms of mp 169—171.5° (from EtOH) from **10b** (84 mg) by the above procedure. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2230 (C≡N). NMR (60 MHz) δ: 7.11 (1H, s, 4-H), 6.90 (1H, s, 10-H), 6.73 (1H, s, 7-H), 6.65 (1H, s, 1-H), 5.98 (2H, s, OCH_2O), 4.86 (1H, s, 6-H), 4.51 (1H, s, 4b-H), 3.94 (3H, s, OMe), 3.90 (3H, s, OMe), 3.13—2.82 (2H, m, 12-H_2), 2.61 (3H, s, 5-Me), 2.19—1.71 (2H, m, 11-H_2), 1.24 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{23}H_{24}N_2O_4 \cdot 1/4H_2O$: C, 69.58; H, 6.23; N, 7.06. Found: C, 69.87; H, 6.26; N, 6.81. MS *m/e*: M^+, 392.174 (M, 392.174).

5,10b-Dimethyl-8,9-methylenedioxy-6-oxo-*cis*-4b,5,6,10b,11,12-hexahydrobenzo[*c*]phenanthridine (15a) and 2,3-Dimethoxy-5,10b-dimethyl-8,9-methylenedioxy-6-oxo-*cis*-4b,5,6,10b,11,12-hexahydrobenzo[*c*]phenanthridine (15b)——1) To a solution of **14a** (70 mg) in ethanol (6 ml) was added a solution of $K_3Fe(CN)_6$ (300 mg) and KOH (150 mg) in H_2O (5 ml). The reaction mixture was refluxed for 1.5 hr under N_2. After cooling, the precipitate was collected and recrystallized from ethanol to give **15a** (62 mg, 91%) as colorless prisms of mp 250°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1638 (NC=O). NMR (100 MHz) δ: 7.40 (1H, s, 7-H), 7.23—6.88 (4H, m, 1-, 2-, 3- and 4-H), 6.71 (1H, s, 10-H), 5.91, 5.87 (2H, each d, J 1.5 Hz, OCH_2O), 4.25 (1H, s, 4b-H), 3.46 (3H, s, 5-Me), 2.92—2.76 (2H, m, 12-H_2), 2.44 (1H, ddd, J 14, 6 and 4 Hz, 11-H), 2.00 (1H, ddd, J 14, 10 and 8 Hz, 11-H), 1.35 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.77; H, 5.98; N, 4.31. MS *m/e*: M^+, 321.135 (M, 321.137).

2) The *cis*-lactam (**15b**) was obtained as colorless needles of mp 202—204° (from EtOH) in quantitative yield from **14b** (32 mg) by the above procedure. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1638 (NC=O). NMR (60 MHz) δ: 7.39 (1H, s, 7-H), 6.72 (1H, s, 10-H), 6.63 (1H, s, 4-H), 6.40 (1H, s, 1-H), 5.90 (2H, s, OCH_2O), 4.21 (1H, s, 4b-H), 3.80 (3H, s, OMe), 3.75 (3H, s, OMe), 3.48 (3H, s, 5-Me), 2.90—2.62 (2H, m, 12-H_2), 2.39—1.82 (2H, m, 11-H_2), 1.33 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{22}H_{23}NO_5$: C, 69.27; H, 6.09; N, 3.67. Found: C, 69.11; H, 6.11; N, 3.73.

2,3-Dimethoxy-5,10b-dimethyl-8,9-methylenedioxy-6-oxo-*trans*-4b,5,6,10b,11,12-hexahydrobenzo[*c*]phenanthridine (17b) and 2,3-Dimethoxy-10b-methyl-8,9-methylenedioxy-5-oxa-6-oxo-4b,5,6,10b,11,12-hexahydrochrysene (13b)——To a solution of **16b** (64 mg) in ethanol (30 ml) was added a solution of $K_3Fe(CN)_6$ (290 mg) and KOH (135 mg) in H_2O (10 ml) and the reaction mixture was refluxed for 1 hr. After cooling, the reaction mixture was diluted with H_2O and extracted with ethyl acetate. The residue (49 mg) obtained from the ethyl acetate layer was purified by preparative TLC (silica gel plates; benzene–ethyl acetate=1:1, v/v) to give **17b** (28 mg, 45%) and **13b** (13 mg, 22%).

The *trans*-Lactam (**17b**): Colorless plates of mp 248—253° (from EtOH). *Rf* 0.42. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1635 (NC=O). NMR (60 MHz) δ: 7.52 (1H, s, 7-H), 6.75 (2H, s, 4- and 10-H), 6.64 (1H, s, 1-H), 5.98 (2H, s, OCH_2O), 4.89 (1H, s, 4b-H), 3.88 (3H, s, OMe), 3.85 (3H, s, OMe), 3.14 (3H, s, 5-Me), 2.93—2.71 (2H, m, 12-H_2), 2.52—1.72 (2H, m, 11-H_2), 1.08 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{22}H_{23}NO_5$: C, 69.27; H, 6.09; N, 3.67. Found: C, 69.04; H, 6.13; N, 3.51.

The Lactone (**13b**): Colorless plates of mp 192—197° (from EtOH). *Rf* 0.69. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1712 (OC=O). NMR (60 MHz) δ: 7.55 (1H, s, 7-H), 7.21 (1H, s, 4-H), 6.83 (1H, s, 10-H), 6.63 (1H, s, 1-H), 6.04 (2H, s, OCH_2O), 5.28 (1H, s, 4b-H), 3.92 (3H, s, OMe), 3.86 (3H, s, OMe), 2.98 (2H, dd, J 10 and 4 Hz, 12-H_2), 2.56—1.60 (2H, m, 11-H_2), 1.11 (3H, s, 10b-Me). *Anal.* Calcd. for $C_{21}H_{20}O_6$: C, 68.46; H, 5.48. Found: C, 68.53; H, 5.46.

2-Methyl-2-(3′,4′-methylenedioxyphenyl)-1-oxo-1,2-dihydronaphthalene (20)——A solution of **2a** (670 mg), NBS (425 mg) and benzoyl peroxide (10 mg) in carbon tetrachloride (30 ml) was refluxed for 4.75 hr. After each 1.5 hr, NBS (100 mg) was added. The reaction mixture was washed with dil. aq. KI solution, dil. aq. $Na_2S_2O_3$ solution and H_2O. The carbon tetrachloride layer gave an oil (1.0 g) containing **19** which was dehydrobrominated by refluxing a solution of DBU (2 ml) in dry toluene (30 ml) for 1.5 hr. The reaction mixture was washed with 10% HCl, 10% aq. NaOH solution and H_2O. The residue (630 mg) obtained from

the toluene layer was purified by column chromatography (Al_2O_3, grade III; 45 g) using benzene-hexane (1: 2, v/v) as solvent to give **20** (381 mg, 57%) as a colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1675 (C=O), 1642 (C=C). NMR (100 MHz) δ: 7.98 (1H, dd, J 8 and 2 Hz, 8-H), 7.65—7.22 (3H, m, 5-, 6- and 7-H), 6.89—6.64 (3H, m, 2'-, 5'- and 6'-H), 6.70 (1H, d, J 10 Hz, 4-H), 6.22 (1H, d, J 10 Hz, 3-H), 5.87 (2H, s, OCH_2O), 1.64 (3H, s, 2-Me). MS m/e: M^+, 278.092. Calcd. for $C_{18}H_{14}O_3$: M, 278.094.

1-Formamido-2-methyl-2-(3',4'-methylenedioxyphenyl)-1,2-dihydronaphthalenes (21 and 22)——A mixture of **20** (225 mg), formamide (3 ml), formic acid (0.3 ml) and $(NH_4)_2SO_4$ (50 mg) was heated at 180—190° for 8 hr. After each 2 hr, formic acid (0.3 ml) was added. The reaction mixture was diluted with H_2O and extracted with ethyl acetate. The residue (270 mg) obtained from the ethyl acetate layer purified by preparative TLC (silica gel plates; benzene–ethyl acetate=4: 1, v/v) to give **21** (130 mg, 52%) and **22** (75 mg, 30%).

The *cis*-Amide (**21**): A colorless oil. *Rf* 0.41. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420 (NH), 1685 (NC=O). NMR (60 MHz) δ: 8.11 (1H, s, CHO), 7.18—7.08 (4H, m, 5-, 6-, 7- and 8-H), 6.75 (1H, s, 2'-H), 6.68 (2H, s, 5'- and 6'-H), 6.60 (1H, d, J 10 Hz, 4-H), 5.96 (1H, d, J 10 Hz, 3-H), 5.85 (2H, s, OCH_2O), 5.62—5.34 (1H, br s, NH), 5.51 (1H, s, 1-H), 1.53 (3H, s, 2-Me). MS m/e: M^+, 307.118. Calcd. for $C_{19}H_{17}NO_3$: M, 307.121.

The *trans*-Amide (**22**): A colorless oil. *Rf* 0.33. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420 (NH), 1685 (NC=O). NMR (60 MHz) δ: 8.15 (1H, s, CHO), 7.18—7.05 (4H, m, 5-, 6-, 7- and 8-H), 6.92—6.62 (4H, m, 4-, 2'-, and 5'- and 6'-H), 5.95 (1H, d, J 10 Hz, 3-H), *ca.* 5.90 (1H, overlapped with the 3-H and OCH_2O signals, NH), 5.85 (2H, s, OCH_2O), 5.49 (1H, d, J 10 Hz, 1-H), 1.43 (3H, s, 2-Me). MS m/e: M^+, 307.122. Calcd. for $C_{19}H_{17}NO_3$: M, 307.121.

10b-Methyl-8,9-methylenedioxy-4b,10b-dihydrobenzo[*c*]phenanthridines (23 and 24)——1) A solution of **21** (81 mg) and $POCl_3$ (0.2 ml) in dry toluene (2 ml) was stirred at room temperature for 4 hr. The work-up gave an oil (77 mg) which was purified by preparative TLC (silica gel plates; benzene–ethyl acetate=5: 1, v/v) to give **23** (44 mg, 58%) as a yellow oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1636 (C=N). NMR (100 MHz) δ: 8.30 (1H, d, J 3 Hz, 6-H), 7.39 (1H, dd, J 9 and 3 Hz, 4-H), 7.32—6.94 (3H, m, 1-, 2- and 3-H), 6.83 (1H, s, 7-H), 6.71 (1H, s, 10-H), 6.51 (1H, d, J 10 Hz, 12-H), 5.92, 5.88 (2H, each d, J 1 Hz, OCH_2O), 5.83 (1H, d, J 10 Hz, 11-H), 4.76 (1H, d, J 3 Hz, 4b-H), 1.37 (3H, s, 10b-Me). MS m/e: M^+, 289.113. Calcd. for $C_{19}H_{15}NO_2$: M, 289.110.

The *cis*-Methiodide (**25**): Yellow crystals of mp 241—242° (from benzene-chloroform). *Anal.* Calcd. for $C_{20}H_{18}INO_2 \cdot 1/4H_2O$: C, 55.12; H, 4.28; N, 3.21. Found: C, 55.14; H, 4.21; N, 3.07.

2) The *trans*-imine (**24**) (20 mg, 43%) was obtained as light yellow crystals of mp 131—132° (from EtOH) from **22** (49 mg) by the above procedure. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1633 (C=N). NMR (100 MHz) δ: 8.43 (1H, d, J 3 Hz, 6-H), 8.14 (1H, dd, J 6 and 2 Hz, 4-H), 7.46—7.06 (3H, m, 1-, 2- and 3-H), 7.06 (1H, s, 10-H), 6.90 (1H, s, 7-H), 6.60 (1H, d, J 10 Hz, 11-H), 6.50 (1H, d, J 10 Hz, 12-H), 6.02 (2H, s, OCH_2O), 4.59 (1H, d, J 3 Hz, 4b-H), 0.82 (3H, s, 10b-Me). MS m/e: M^+, 289.109. Calcd. for $C_{19}H_{15}NO_2$: M, 289.110.

5,10b-Dimethyl-8,9-methylenedioxy-*cis*-4b,5,6,10b-tetrahydrobenzo[*c*]phenanthridine (26)——To a solution of **25** (15 mg) in methanol (0.5 ml) was added $NaBH_4$ (4 mg) and the reaction mixture was stirred at room temperature for 10 min. The work-up afforded crystals (10 mg) which were purified by preparative TLC (silica gel plates; benzene–ethyl acetate=5: 1, v/v) to give **26** (9 mg, 84%) as colorless needles of mp 152—153° (from ether–hexane). NMR (100 MHz) δ: 7.38—7.02 (4H, m, 1-, 2-, 3- and 4-H), 6.91 (1H, s, 10-H), 6.49 (1H, s, 7-H), 6.40 (1H, d, J 10 Hz, 12-H), 5.92 (1H, dd, J 10 and 2 Hz, 11-H), 5.92 (2H, s, OCH_2O), 3.81 (1H, d, J 15 Hz, 6-H), 3.65 (1H, d, J 15 Hz, 6-H), 3.24 (1H, d, J 2 Hz, 4b-H), 2.05 (3H, s, 5-Me), 1.23 (3H, s, 10b-Me). MS m/e: M^+, 305.140. Calcd. for $C_{20}H_{19}NO_2$: M, 305.142.