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Utilization of Protopine and Related Alkaloids. XIV.[1] Oxidation of the Photo-adduct of 1-Oxoanhydromethylberberine with Nitrosobenzene, and Synthesis of Ring C-Substituted Benzo[*c*]phenanthridines

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Oxidation of the photo-adduct (**2**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone under anhydrous conditions gives the imine (**3**) and the aniline (**4**). The oxidation of **2** in the presence of water and anhydrous methanol affords the 1-oxo-2β,4β-epoxyimine (**6**) and the 4bα-methoxy-10bβ,12β-epoxyimine (**8**), respectively. The mechanisms of formation of these compounds are discussed. The quinone (**5**), derived from **3** and **4**, is reduced with sodium borohydride to yield the *cis*-diol (**25**) and the *trans*-diol (**26**). On reduction with lithium aluminum hydride and subsequent hydrogenation over palladium-carbon, **8** gives the 4bβH-12β-anilino-10bβ-ol (**33**) and the 4bαH isomer (**34**).

Keywords——benzo[*c*]phenanthridine; oxidation; reaction mechanism; IR absorption (Bohlmann band); ^{1}HNMR; ^{13}CNMR

We previously reported that the photolysis of 1-oxoanhydroberberine (**1**),[2] derived from α-allocryptopine or berberinium chloride, in the presence of nitrosobenzene gave 4b,10bβ,11,12-tetrahydro-4bβ,12β-(*N*-phenylepoxyimino)oxychelerythrine (**2**),[3] and that attempts to obtain homochelidonine from **2** were unsuccessful.[1] In this paper, we report interesting findings obtained during further investigations on the synthesis of benzo[*c*]phenanthridine alkaloids from **2**.

Oxidation of **2** with an equimolar amount of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in anhydrous dichloromethane gave the imine (**3**) (33%), the aniline (**4**) (29%) and the quinone (**5**) (6%). Since formation of **5** was observed during preparative thin-layer chromatography (prep. TLC) of the oxidative products, **5** is not the primary product. The proton magnetic resonance (^{1}H NMR) spectrum of **3** showed that the 1- and 10-protons were deshielded by the 12-phenylimino and 11-oxo groups, and resonated at δ 7.55 (s) and 8.53 (d, J 8 Hz), respectively. Hydrolysis of **3** with hydrochloric acid afforded **5** (77%) [^{1}H NMR: δ 7.46 (s, 1-H) and 9.00 (d, J 9 Hz, 10-H)]. The aniline (**4**) was identified by direct comparison with an authentic sample.[3]

The DDQ oxidation of **2** in the presence of water and anhydrous methanol gave the 1-oxo-2β,4β-epoxyimine (**6**) (63%) and the 4bα-methoxy-10bβ,12β-epoxyimine (**8**) (72%), respectively. The infrared (IR) spectrum of **6** exhibited two carbonyl bands at 1690 (C=O) and 1655 cm^{-1} (NC=O). The ^{1}H NMR spectrum showed an ABX spin system [δ 3.09 (1H, dd, J 12 and 0.5 Hz, 3-H), 2.85 (1H, dd, J 12 and 4.5 Hz, 3-H) and 5.02 (1H, dd, J 4.5 and 0.5 Hz, 4-H)] and a methylcarbamoyl group [δ 6.09 (1H, br s, W_H 20 Hz, 2′-CONHMe)[4] and 2.79 (3H, d, J 5 Hz, 2′-CONHMe)[5]]. A methylene carbon (C-3) and a methine carbon (C-4) corresponding to the ABX proton spin system were observed at δ 45.3 and 68.5, respectively, in the ^{13}C NMR spectrum. Also, three quaternary carbons were detected at δ 191.1 (C-1), 168.1 (2′-CONHMe) and 88.5 (C-2). These spectral data are consistent with the structure proposed for **6**. On reduction with sodium borohydride, **6** exclusively gave the 1β-hydroxy-2β,4β-epoxyimine (**7**) [IR: 3565 cm^{-1} (OH……O)].[1,6] From a comparison of the NMR (^{1}H and ^{13}C) data for **8** with those for **6**, it is clear that **8** is a benzo[*c*]phenanthridine containing a methoxyl group at the 4b-position and an epoxyimino group at the 10b- and 12-positions (see "Experimental"). It is known that the 5-methyl protons in *cis*-and *trans*-4b,5,6,10b,11,12-hexahydro-6-oxobenzo-

[*c*]phenanthridines resonate at δ *ca.* 3.50 and *ca.* 3.15, respectively.[7] Since a three-proton singlet observed at δ 3.22 is assigned to the 5-methyl protons, the B/C ring juncture in **8** is thought to be *trans*. Treatment of **8** with hydrochloric acid gave **6** (67%).

We now consider the reaction pathways. From comparison of the molecular formulae, it can be seen that **3**, $C_{27}H_{20}N_2O_6$, is formed by further oxidation of an oxidative product of **2**,

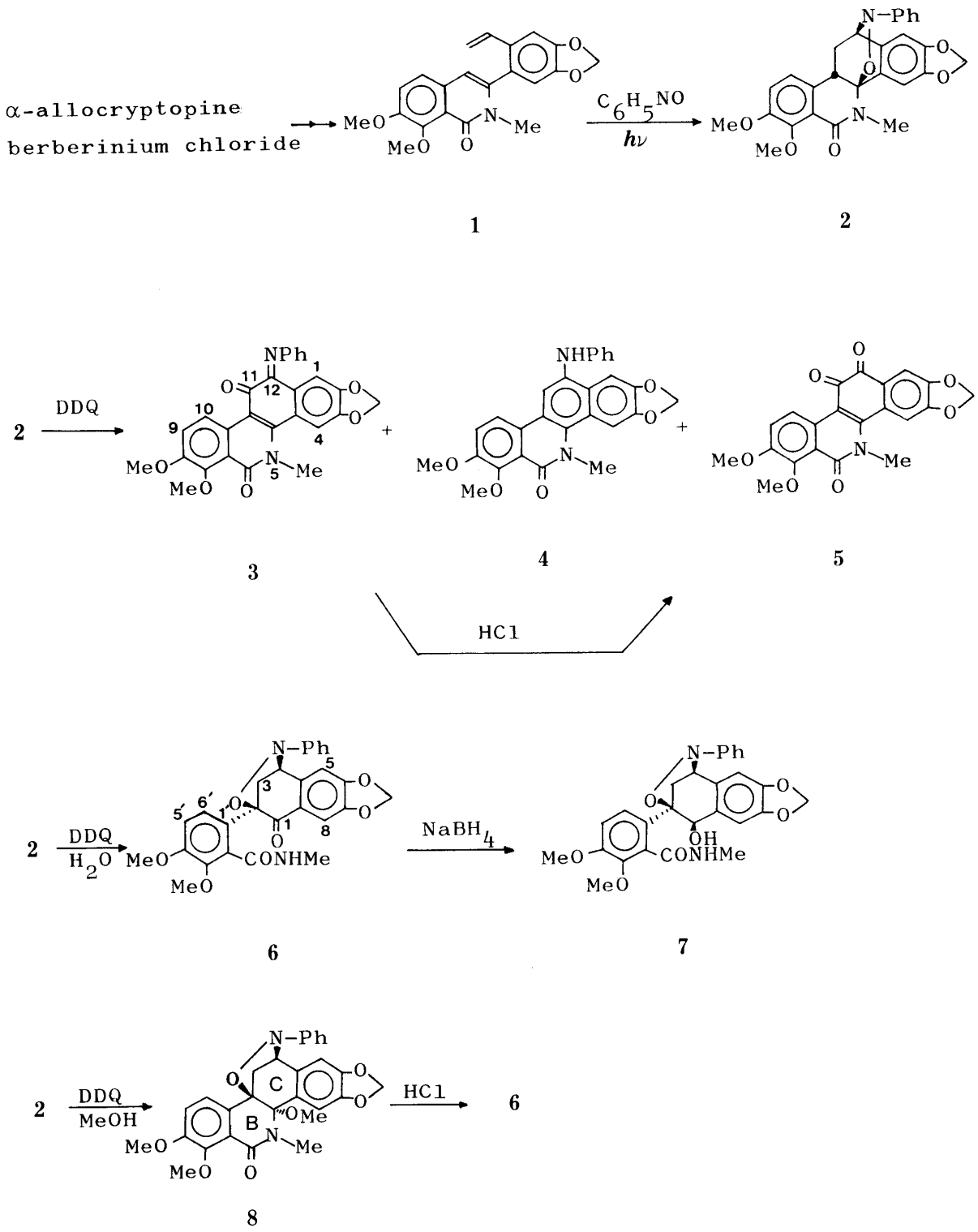


Chart 1

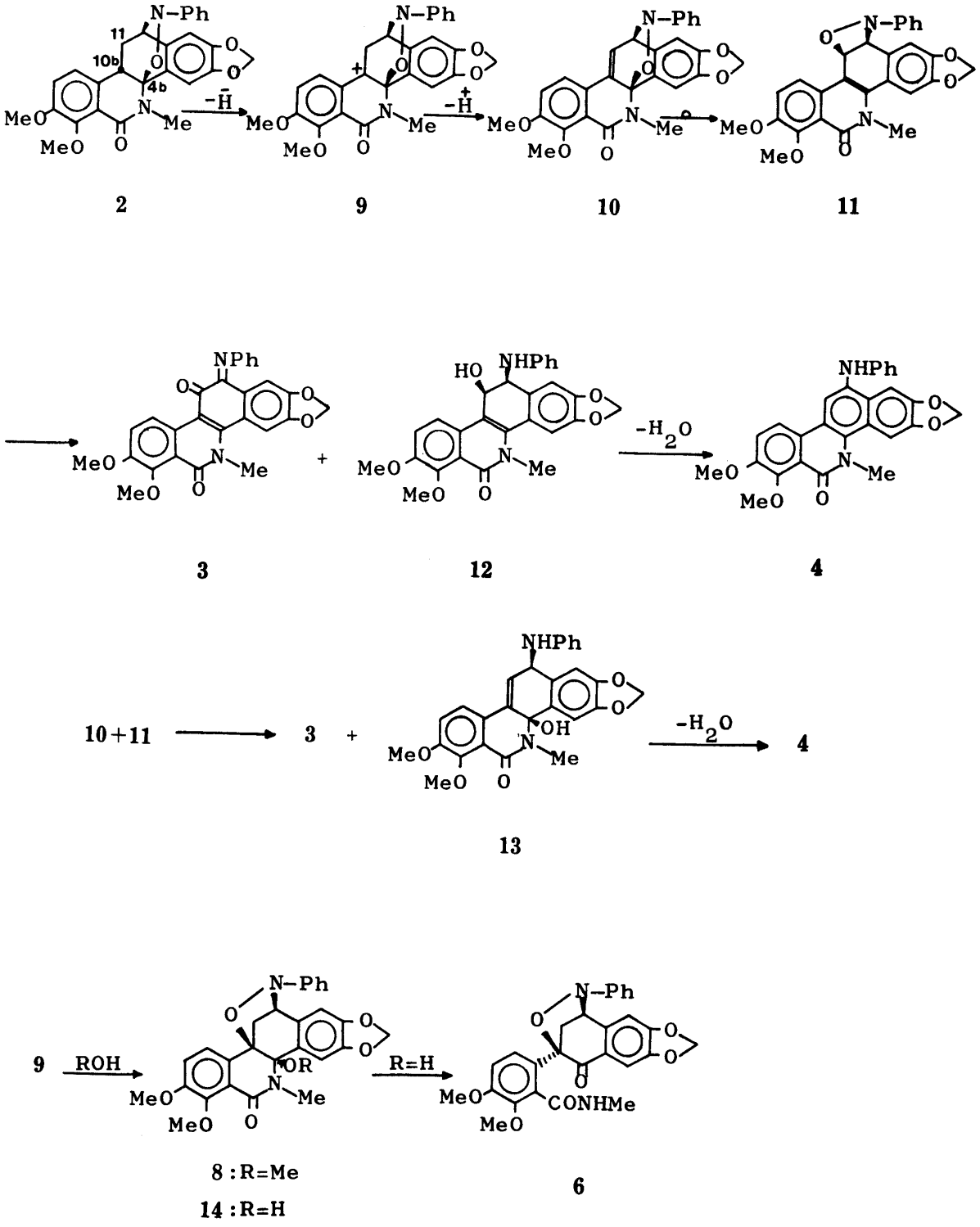
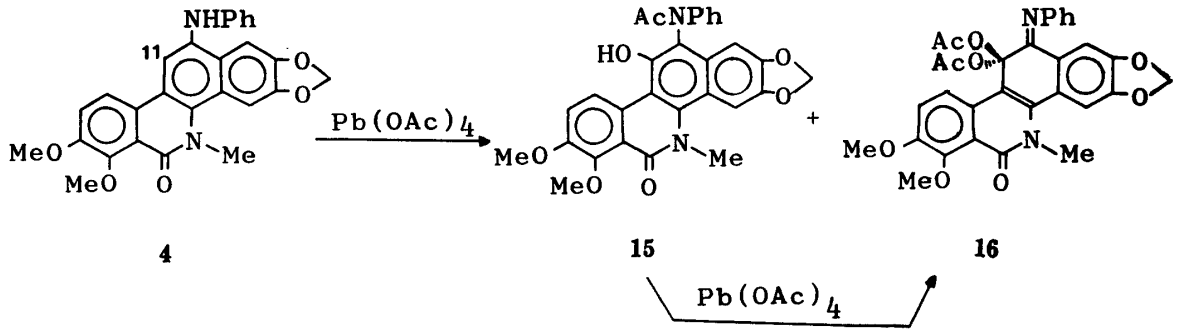


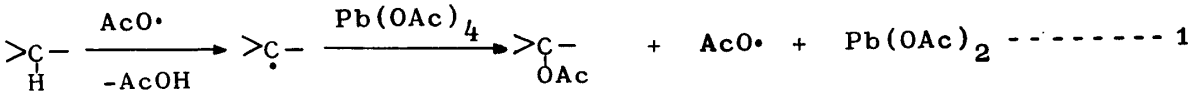
Chart 2

$C_{27}H_{24}N_2O_6$, and that **4**, $C_{27}H_{22}N_2O_5$, is produced by elimination of water from an intermediate formed by reduction of an oxidative product of **2**. Taking into account the amount of DDQ added, disproportionation of an intermediate and/or a similar reaction between two different intermediates must have occurred during the formation of **3** and **4**. A possible first step in the oxidation is thought to be abstraction of a hydride ion from the 10b-position in **2** to give the cation (**9**).[8] Successive abstraction of a proton from the 11-position in **9** affords the *cis*-4b,12-

epoxyimine (**10**), which would be converted by allylic rearrangement into the *cis*-11,12-epoxyimine (**11**). Disproportionation of **11** would afford **3** and the *cis*-12-anilino-11-ol (**12**), the latter of which gives **4** by elimination of water. Alternatively, a similar reaction between **10** and **11** could afford **3** and the *cis*-12-anilino-4b-ol (**13**), the latter of which is converted by elimination of water into **4**. The presence of methanol and water in the oxidation system changed the reaction pathway. These reagents would attack the 4b-position in **9**,[8] accompanied by a concerted shift of the oxygen atom at the 4b-position to the 10b-position to give **8** and a similar compound (**14**), respectively, the latter of which is converted into **6**.

Oxidation of **4** with one-half equimolar amount of lead tetraacetate[9] gave the acetanilido phenol (**15**) (41%) and the diacetoxy imine (**16**) (4%), accompanied by recovery of **4** (28%). The IR spectrum of **15** showed bands at 3550 (OH) and 1645 cm^{-1} (NC=O). Further oxidation of **15** with one-half equimolar amount of lead tetraacetate afforded **16** (99%). Oxidation of **4** with an equimolar amount of lead tetraacetate gave **16** (73%), which was identified by direct comparison with an authentic sample.[3] These results suggest that the reaction mechanism is different from that (equation 1) depicted in Chart 3. A possible first step in the oxidation is thought to be acetoxylation at the 11-position in **4** to yield the acetoxy aniline (**17**),[10] which is converted by acetyl migration into **15**. Formation of **16** would arise from acetyl migration in the radical (**18**) derived by acetoxylation at the 11-position in **15**. In the case of the use of





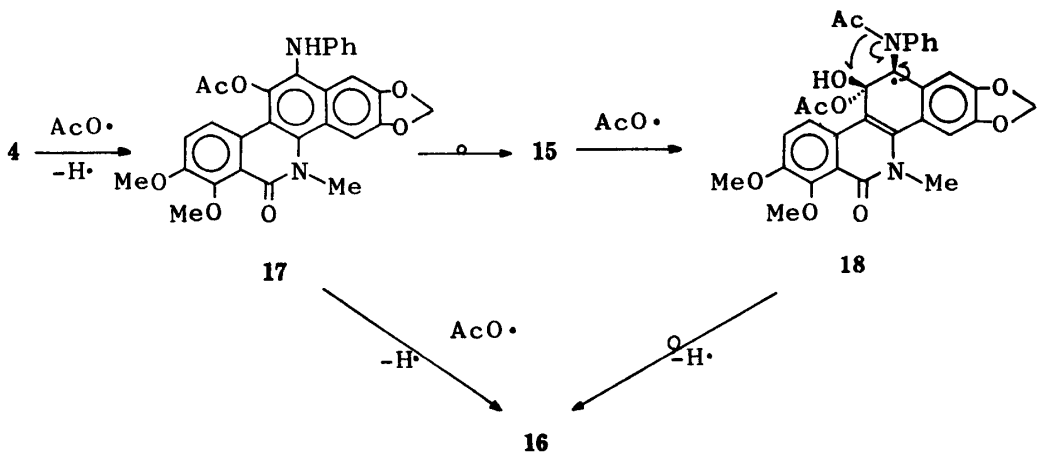


Chart 3

an equimolar amount of lead tetraacetate for **4**, it is also likely that **16** is directly formed by acetoxylation at the 11-position in **17**.

Reduction of **3** with lithium aluminum hydride gave the 12ξ-anilino-11β-ol (**19**) (84%) [IR: 3400 cm^{-1} (NH and OH). ^1H NMR: δ 5.19 and 4.67 (d each, J 3 Hz, 11- and 12-H's)]. Treatment of **19** with hydrochloric acid and acetic anhydride afforded **4** (93%) and the acetanilide (**20**) (86%), respectively, the latter of which was identified by direct comparison with an authentic sample.[3] Oxidation of **19** with DDQ gave the imino aldehyde (**21**) (81%) [^1H NMR: δ 9.54 (s, 4-CHO) and 8.13 (s, 2'-C<u>H</u>=NPh)], which was converted by hydrolysis with hydrochloric acid into the dicarbaldehyde (**22**) (95%) [^1H NMR: δ 9.74 and 9.43 (s each, 4- and 2'-CHO's)].

Reduction of **16** with lithium aluminum hydride/aluminum chloride, unusually, afforded 5,6-dihydrochelerythrine (**23**) (35%) and 5,6-dihydro-7-demethoxychelerythrine (**24**) (32%) [^1H NMR: δ 6.82 (d, J 3 Hz, 7-H)]. Identification of **23** was carried out by direct comparison with an authentic sample.[2]

Hydrolysis of **16** with hydrochloric acid gave the quinone (**5**) (69%). On reduction with sodium borohydride, **5** afforded the *cis*-diol (**25**) (17%) and the *trans*-diol (**26**) (19%), which were acetylated with acetic anhydride to yield the *cis*-diacetate (**27**) (84%) and the *trans*-diacetate (**28**) (99%), respectively. The ^1H NMR spectrum of **27** showed a doublet due to the 1-proton at δ 6.93 (J 1.5 Hz) and a double doublet due to the 12-proton at δ 6.13 (J 4 and 1.5 Hz). Decoupling experiments verified that these protons were mutually coupled (J 1.5 Hz), and thus suggest that the 12-proton is oriented axially.[11] A nuclear Overhauser effect (NOE) (9%) observed between these protons is in accord with the internuclear distance (*ca.* 3.2 Å) between the 1- and 12_{ax}-protons assessed from a Dreiding model.[12] The ^1H NMR spectrum of **28** exhibited a singlet due to the 1-proton at δ 7.07 and a doublet due to the 12-proton at δ 5.68 (J 3 Hz). An NOE (20%) observed between these protons corresponds to the internuclear distance (*ca.* 2.4 Å) between the 1- and 12_{eq}-protons.[12] Saturation of the 10- and 11-protons in **27** and **28** caused *ca.* 21% and *ca.* 15% area increases in the signals of the 11- and 10-protons, respectively. The NOE's observed are in accord with the internuclear distances (*ca.* 2.1 Å) between the 10- and 11_{eq}-protons.[13] From these results and coupling constants observed between the 11- and 12-protons, the configurations of the 11- and 12-acetoxy groups in **27** and **28** can be assigned as follows: **27**, 11_{ax}- and 12_{eq}-OAc's; **28**, 11_{ax}- and 12_{ax}-OAc's.

The *trans*-diol (**26**) gave 12-methoxyoxychelerythrine (**29**) (99%) on treatment with hydrochloric acid and successive methylation with diazomethane. Treatment of **28** with hydrochloric acid afforded 12-acetoxychelerythrine (**30**) (85%). The positions of the methoxyl and acetoxy groups in **29** and **30** were established by comparison of the chemical shifts of the 10-protons in these compounds with that [δ 7.88 (d, J 8 Hz)] of the 10-proton in oxychelerythrine[14] [**29**: δ 7.89 (d, J 9 Hz). **30**: δ 7.82 (d, J 9 Hz)].[15]

Reduction of **8** with lithium aluminum hydride gave a mixture of the 4bβ<u>H</u>-10bβ,12β-epoxyimine (**31**) and the 4bα<u>H</u> isomer (**32**) in an approximate ratio of 2/1, as estimated from the 5-methyl proton signal areas in the ^1H NMR spectra. Prep. TLC of the mixture afforded **31** (35%) and **32** (18%), which gave the 4bβ<u>H</u>-12β-anilino-10bβ-ol (**33**) (56%) and the 4bαH isomer (**34**) (69%), respectively, on hydrogenation over palladium-carbon. As expected, the IR spectra of **33** and **34** showed intramolecular hydrogen-bondings (OH····N) at 3390 and 3395 cm^{-1}, respectively.[16] Also, Bohlmann bands were observed at 2768 cm^{-1} with molar absorptivities of 138 and 54 for **33** and **34**, respectively. The characteristic ^1H NMR signals are as follows: **33**, δ 4.02, 3.53 (1H each, d, J 17 Hz, 6-H_2), 3.40 (1H, s, 4b-H) and 2.38 (3H, s, 5-Me); **34**, δ 7.29 (1H, s, 4-H), 4.31, 3.90 (1H each, d, J 17 Hz, 6-H_2), 4.20 (1H, s, 4b-H) and 2.55 (3H, s, 5-Me)]. These spectral data are in accord with those for the *cis* (steroidal) and *trans* isomers of 4b,5,6,10b,11,12-hexahydrobenzo[*c*]phenanthridines.[17] Deviations of the spectral data for **31** and **32** are thought to be ascribable to deformation of the B rings caused by the 10b,12-epoxyimino groups (see "Experimental").

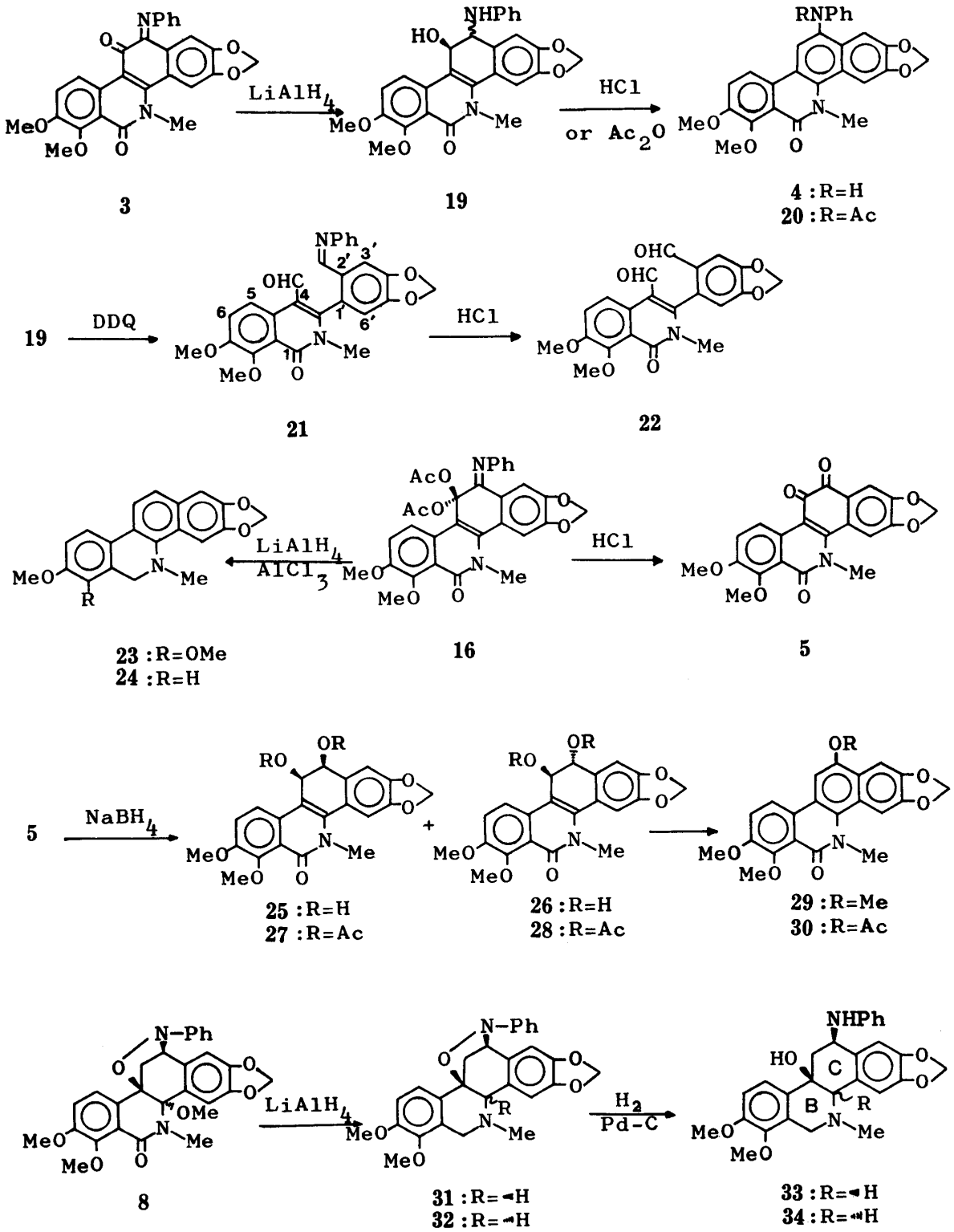


Chart 4

Experimental

Melting points were determined on a micro hot-stage apparatus and are uncorrected. Spectral data were recorded on the following spectrometers: IR—JASCO IR-G (in chloroform) and JASCO DS-701G (hydrogen-bondings and Bohlmann bands) (in tetrachloromethane): ^{1}H NMR—JEOL JNM PS-100 (100

MHz) and Varian EM-390 (90 MHz) (in deuteriochloroform unless otherwise noted); ^{13}C NMR—JEOL JNM PS-100 (25.1 MHz) (in deuteriochloroform); mass (MS)—JEOL JM-01S. Prep. TLC's were performed on silica gel plates.

11,12-Dihydro-11-oxo-12-phenyliminooxychelerythrine (3), 12-Anilinooxychelerythrine (4) and 11,12-Dihydro-11,12-dioxooxychelerythrine (5)——A solution of DDQ (54.0 mg) in anhydrous dichloromethane (4 ml) was added to a solution of **2** (100.9 mg) in anhydrous dichloromethane (2 ml), and the mixture was stirred at 45°C for 30 min. The organic phase was washed with 10% aqueous Na_2CO_3 (A) and water, then dried over Na_2SO_4 and filtered. Removal of the solvent *in vacuo* gave a brown oil (114.3 mg), which was purified by prep. TLC (chloroform/ethyl acetate=2/1, v/v) to yield **3** (33.3 mg, 33%), **4** (28.5 mg, 29%) and **5** (4.9 mg, 6%) from the zones with *Rf* 0.37, 0.30 and 0.21, respectively.

The Imine (**3**): Red granules of mp 196—198°C (from ether). IR ν_{max} cm^{-1}: 1675 (C=O), 1655 (NC=O). ^1H NMR (100 MHz) δ: 8.53 (1H, d, *J* 8 Hz, 10-H), 7.55 (1H, s, 1-H), 7.44—7.12 (3H, m, aromatic H's), 7.02 (1H, s, 4-H), 6.95—6.80 (3H, m, aromatic H's), 6.10 (2H, s, 2,3-OCH_2O–), 3.98 (3H, s, 7-OMe), 3.91 (3H, s, 8-OMe), 3.78 (3H, s, 5-Me). MS Calcd for $C_{27}H_{20}N_2O_6$: M, 468.132. Found *m/z*: M^+, 468.132.

The Aniline (**4**): Light yellow granules of mp 170—173°C (from ether). IR ν_{max} cm^{-1}: 3400 (NH), 1640 (NC=O). ^1H NMR (100 MHz) δ: 7.90 (1H, s, 11-H), 7.79 (1H, d, *J* 8 Hz, 10-H), 7.52 (1H, s, 4-H), 7.39 (1H, s, 1-H), 7.30 (1H, d, *J* 8 Hz, 9-H), 7.30—7.15 (2H, m, aromatic H's), 6.91—6.73 (3H, m, aromatic H's), 6.05 (2H, s, 2,3-OCH_2O–), 5.66 (1H, s, 12-N<u>H</u>Ph),[4] 4.06 (3H, s, 7-OMe), 3.94 (3H, s, 8-OMe), 3.88 (3H, s, 5-Me). MS Calcd for $C_{27}H_{22}N_2O_5$: M, 454.153. Found *m/z*: M^+, 454.153.

The Quinone (**5**): Violet granules of mp 279—280°C (washed with ether). This compound was not recrystallized because of its insolubility in common solvents. IR ν_{max} cm^{-1}: 1695, 1680 (C=O), 1650 (NC=O). ^1H NMR (100 MHz) δ: 9.00 (1H, d, *J* 9 Hz, 10-H), 7.46 (1H, s, 1-H), 7.40 (1H, d, *J* 9 Hz, 9-H), 7.03 (1H, s, 4-H), 6.14 (2H, s, 2,3-OCH_2O–), 4.01 (3H, s, 7-OMe), 3.97 (3H, s, 8-OMe), 3.77 (3H, s, 5-Me). MS Calcd for $C_{21}H_{15}NO_7$: M, 393.085. Found *m/z*: M^+, 393.085.

Acidification of the alkaline washing (A) with 10% HCl gave 2H-DDQ (47.9 mg, 88%) as colorless granules (from ethanol/water), which blackened at 265°C.[18]

2α-3′,4′-Dimethoxy-2′-methylcarbamoylphenyl-6,7-methylenedioxy-2β,4β-(*N*-phenylepoxyimino)-α-tetralone (6)——A solution of DDQ (48.6 mg) in dichloromethane/water (18/1, v/v) (4 ml) was added to a solution of **2** (101.2 mg) in the same solvent (2 ml), and the mixture was stirred at room temperature for 40 min. Work-up of the reaction mixture gave a brown oil (118.6 mg), which was purified by prep. TLC (chloroform/ethyl acetate=2/1, v/v) to yield **6** (66.1 mg, 63%), *Rf* 0.16, as colorless granules of mp 258—260°C (from chloroform/ether), accompanied by an unidentified compound (30.0 mg). IR ν_{max} cm^{-1}: 3425 (NH), 1690 (C=O), 1655 (NC=O). ^1H NMR (100 MHz) δ: 7.61 (1H, d, *J* 8 Hz, 6′-H), 7.47 (1H, s, 8-H), 7.20—6.91 (6H, m, aromatic H's), 6.73 (1H, s, 5-H), 6.09 (1H, br s, W_H 20 Hz, 2′-CON<u>H</u>Me),[4] 6.02, 5.99 (1H each, d, *J* 1 Hz, 6,7-OCH_2O–), 5.02 (1H, dd, *J* 4.5 and 0.5 Hz, 4-H), 3.91 (3H, s, 3′-OMe), 3.87 (3H, s, 4′-OMe), 3.09 (1H, dd, *J* 12 and 0.5 Hz, 3-H), 2.85 (1H, dd, *J* 12 and 4.5 Hz, 3-H), 2.79 (3H, d, *J* 5 Hz, 2′-CONH<u>Me</u>).[5] Decoupling: δ 5.02 (4-H)→δ 3.09 (dd→d, *J* 12 Hz, 3-H), 2.85 (dd→d, *J* 12 Hz, 3-H). ^{13}C NMR δ: 191.1 (s, C-1), 168.1 (s, 2′-<u>C</u>ONHMe), 153.0 (s, C-4′), 152.7, 149.7 (s each, C-6 and -7), 148.8 (s, C-1″), 146.5 (s, C-3′), 138.8 (s, C-1′), 131.4 (s, C-4a), 129.1 (d, C-3″ and -5″), 127.0, 126.2 (s each, C-8a and -2′), 123.8 (d, C-4″), 123.3 (s, C-6′), 117.5 (d, C-2″ and -6″), 113.3 (d, C-5′), 107.9, 107.7 (d each, C-5 and -8), 102.4 (t, 6,7-OCH_2O–), 88.5 (s, C-2), 68.5 (d, C-4), 62.1 (q, 3′-OMe), 56.1 (q, 4′-OMe), 45.3 (t, C-3), 26.7 (q, 2′-CONH<u>Me</u>). MS Calcd for $C_{27}H_{24}N_2O_7$: M, 488.158. Found *m/z*: M^+, 488.156.

1,2,3,4-Tetrahydro-1β-hydroxy-2α-3′,4′-dimethoxy-2′-methylcarbamoylphenyl-6,7-methylenedioxy-2β,4β-(*N*-phenylepoxyimino)naphthalene (7)——$NaBH_4$ (13.0 mg) was added to a solution of **6** (40.0 mg) in chloroform (5 ml) and methanol (5 ml), and the mixture was stirred at −40°C for 2 h. After addition of acetic acid (0.05 ml), the reaction mixture was worked up to yield yellow crystals (42.0 mg), which were purified by prep. TLC (benzene/ethyl acetate=1/1, v/v) to yield **7** (39.8 mg, 99%), *Rf* 0.26, as colorless granules of mp 157—159°C (from methanol). IR ν_{max} cm^{-1} ($c=9.17\times10^{-4}$ mol/l): 3565 (ε=43) (OH···O), 3456 (NH), 1672 (NC=O). ^1H NMR (90 MHz) δ: 7.34 (1H, d, *J* 9 Hz, 6′-H), 7.20—6.90 (7H, m, aromatic H's), 6.58 (1H, s, 5-H), 6.03 (1H, q, *J* 5 Hz, 2′-CON<u>H</u>Me),[4] 5.89, 5.86 (1H, each, *J* 1.5 Hz, 6,7-OCH_2O–), 5.03 (1H, s, 1-OH),[4] 4.61 (1H, dd, *J* 4.5 and 0.5, 4-H), 3.87 (4H, s, 1-H and 3′-OMe), 3.80 (3H, s, 4′-OMe), 2.82 (3H, d, *J* 5 Hz, 2′-CONH<u>Me</u>),[5] 2.74 (1H, dd, *J* 12 and 0.5 Hz, 3-H), 2.56 (1H, dd, *J* 12 and 4.5 Hz, 3-H). Decoupling: δ 4.61 (4-H)→δ 2.74 (dd→d, *J* 12 Hz, 3-H), 2.56 (dd→d, *J* 12 Hz, 3-H). MS Calcd for $C_{27}H_{26}N_2O_7$: M, 490.174. Found *m/z*: M^+, 490.174.

4b,10b,11,12-Tetrahydro-4bα-methoxy-10bβ,12β-(*N*-phenylepoxyimino)oxychelerythrine (8)——A solution of DDQ (50.0 mg) in anhydrous dichloromethane/anhydrous methanol (18/1, v/v) (4 ml) was added to a solution of **2** (100.9 mg) in the same solvent (2 ml), and the mixture was stirred at room temperature for 5 min. Work-up of the reaction mixture afforded a brown oil (130.0 mg), which was purified by prep. TLC (benzene/ethyl acetate=1/1, v/v) to yield **8** (77.5 mg, 72%), *Rf* 0.40, as colorless prisms of mp 213—215°C (from ethanol), accompanied by an unidentified compound (26.1 mg), *Rf* 0.35. IR ν_{max} cm^{-1}: 1654 (NC=O). ^1H NMR (90 MHz) δ: 7.56 (1H, d, *J* 9 Hz, 10-H), 7.18—6.92 (7H, m, aromatic H's), 6.60 (1H, s, 1-H), 5.96, 5.91 (1H each, d, *J* 1 Hz, 2,3-OCH_2O–), 4.93 (1H, d, *J* 4 Hz, 12-H), 3.97 (3H, s, 7-OMe), 3.88 (3H, s, 8-OMe), 3.22 (3H, s, 5-Me), 2.99 (1H, d, *J* 12 Hz, 11-H), 2.87 (3H, s, 4b-OMe), 2.52 (1H, dd, *J* 12 and 4 Hz, 11-H). ^{13}C

NMR δ: 163.3 (s, C-6), 154.2 (s, C-8), 150.1, 149.2 (s each, C-2 and -3), 148.6 (s, C-1'), 148.0 (s, C-7), 131.2, 130.3 (s each, C-10a and -12a), 129.1 (d, C-3' and -5'), 126.2 (s, C-4a), 122.8 (d, C-4'), 122.4 (s, C-6a), 119.5 (d, C-10), 116.7 (d, C-2' and -6'), 115.8 (d, C-9), 110.3 (d, C-1), 108.4 (d, C-4), 101.8 (t, 2,3-OCH_2O-), 93.6 (s, C-4b), 88.4 (s, C-10b), 65.4 (d, C-12), 61.7 (q, 7-OMe), 56.3 (q, 8-OMe), 54.7 (q, 4b-OMe), 43.9 (t, C-11), 30.4 (q, 5-Me). *Anal.* Calcd for $C_{28}H_{26}N_2O_7$: C, 66.92; H, 5.22; N, 5.57. Found: C, 66.98; H, 5.29; N, 5.48.

The 1-Oxo-2β,4β-epoxyimine (6) from the 4bα-Methoxy-10bβ,12β-epoxyimine (8)——A solution of **8** (21.4 mg) in methanol (1 ml) containing 10% HCl (1 drop) was stirred at room temperature for 1 h. Work-up of the reaction mixture gave an oil (19.8 mg), which was purified by prep. TLC (benzene/ethyl acetate=1/1, v/v) to yield **6** (13.9 mg, 67%), *Rf* 0.29, as colorless granules of mp 258—260°C (from chloroform/ether).

12-Acetanilido-11-hydroxyoxychelerythrine (15) and 11,11-Diacetoxy-11,12-dihydro-12-phenyliminooxychelerythrine (16)——Pb_3O_4 (22.7 mg) was added to a solution of **4** (30.1 mg) in acetic acid (0.5 ml), and the mixture was stirred at room temperature under N_2 for 1 h. The reaction mixture was diluted with water (10 ml) and extracted with chloroform. Work-up gave yellow crystals (33.3 mg), which were purified by prep. TLC (chloroform/ethyl acetate=2/1, v/v). The yellow crystals, obtained from the zone with *Rf* 0.23 by elution with chloroform, were washed with ether to yield **15** (13.9 mg, 41%) (ether-insoluble) and **16** (1.3 mg, 4%) (ether-soluble). Unreacted **4** (8.3 mg, 28%) was recovered from the zone with *Rf* 0.30.

The Acetanilido Phenol (**15**): Colorless granules of mp 266.5—268.5°C (from chloroform/ether). IR ν_{max} cm^{-1}: 3550 (OH), 1645 (NC=O). ^1H NMR (90 MHz) (dimethyl sufoxide-d_6) δ: 10.35 (1H, s, 11-OH),[4] 9.06 (1H, d, *J* 9 Hz, 10-H), 7.63—7.03 (8H, m, aromatic H's), 6.16, 6.13 (1H each, d, *J* 1 Hz, 2,3-OCH_2O-), 3.92 (3H, s, 7-OMe), 3.88 (3H, s, 8-OMe), 3.70 (3H, s, 5-Me), *ca.* 2.50 (12-NPhCOMe, overlapping with solvent signal). MS Calcd for $C_{29}H_{24}N_2O_7$: M, 512.158. Found *m/z*: M^+, 512.160.

The Diacetoxy Imine (**16**): Yellow granules of mp 160—160.5°C (from methanol). IR ν_{max} cm^{-1}: 1756, 1710 (OC=O), 1645 (NC=O). ^1H NMR (100 MHz) δ: 8.38 (1H, d, *J* 9 Hz, 10-H), 7.40—7.12 (6H, m, aromatic H's), 6.85 (1H, s, 4-H), 6.41 (1H, s, 1-H), 5.89, 5.86 (1H each, d, *J* 1 Hz, 2,3-OCH_2O-), 4.00 (3H, s, 7-OMe), 3.92 (3H, s, 8-OMe), 3.72 (3H, s, 5-Me), 2.30, 1.66 (3H each, s, 11-OCOMe's). MS Calcd for $C_{31}H_{26}N_2O_9$: M, 570.164. Found *m/z*: M^+, 570.163.

The Diacetoxy Imine (16) from the Aniline (4) and the Acetanilido Phenol (15)——*a*) Pb_3O_4 (206.7 mg) was added to a solution of **4** (103.1 mg) in acetic acid (1.5 ml), and the mixture was stirred at room temperature under N_2 for 1 h. After addition of water (30 ml), the reaction mixture was extracted with chloroform. Work-up gave a yellow oil (121.5 mg), which was purified by prep. TLC (chloroform/ethyl acetate=2/1, v/v) to yield **16** (95.0 mg, 73%), *Rf* 0.22, as yellow granules of mp 160—160.5°C (from methanol).

b) Pb_3O_4 (26.8 mg) was added to a solution of **15** (33.0 mg) in acetic acid (0.5 ml), and the mixture was stirred at room temperature under N_2 for 20 min. Work-up of the reaction mixture and prep. TLC (chloroform/ethyl acetate=2/1, v/v) gave **16** (36.5 mg, 99%), *Rf* 0.22, as yellow granules of mp 160—160.5°C (from methanol).

12ξ-Anilino-11,12-dihydro-11β-hydroxyoxychelerythrine (19)——$LiAlH_4$ (111.0 mg) was added to a solution of **3** (167.1 mg) in anhydrous 1,2-dimethoxyethane (34 ml), and the mixture was stirred with cooling under N_2 for 1 h. Work-up of the reaction mixture gave a brown oil (155.9 mg), which was purified by prep. TLC (chloroform/ethyl acetate=2/1, v/v) to yield **19** (141.8 mg, 84%), *Rf* 0.17, as colorless prisms of mp 165—167°C (from chloroform/ether). IR ν_{max} cm^{-1}: 3400 (NH and OH), 1643 (NC=O). ^1H NMR (90 MHz) δ: 7.60 (1H, d, *J* 9 Hz, 10-H), 7.29 (1H, d, *J* 9 Hz, 9-H), 7.19—7.11 (2H, m, aromatic H's), 6.97, 6.94 (1H each, s, 1- and 4-H's), 6.81—6.67 (3H, m, aromatic H's), 5.97 (2H, s, 2,3-OCH_2O-), 5.19, 4.67 (1H each, d, *J* 3 Hz, 11- and 12-H's), 3.97 (3H, s, 7-OMe), 3.88 (3H, s, 8-OMe), 3.66 (3H, s, 5-Me), 2.00, 1.67 (1H each, s, 11-OH and 12-NHPh).[4] MS Calcd for $C_{27}H_{24}N_2O_6$: M, 472.163. Found *m/z*: M^+, 472.164.

Unreacted **3** (12.4 mg, 7%) was recovered from the zone with *Rf* 0.37.

The Aniline (4) from the 12ξ-Anilino-11β-ol (19)——A solution of **19** (5.9 mg) in methanol (1 ml) containing conc. HCl (1 drop) was stirred at 70°C for 5 min. Work-up of the reaction mixture gave **4** (5.3 mg, 93%) as light yellow granules of mp 170—173°C (from ether).

12-Acetanilidooxychelerythrine (20)——A solution of **19** (25.7 mg) in acetic anhydride (1 ml) containing anhydrous pyridine (1 drop) was stirred at room temperature for 18 h. After addition of water (10 ml), the reaction mixture was extracted with chloroform. The residue (27.0 mg), obtained from the organic phase, was purified by prep. TLC (chloroform/ethyl acetate=2/1, v/v) to give **20** (23.2 mg, 86%), *Rf* 0.30, as colorless granules of mp 304—305°C (dec.) (from chloroform). IR ν_{max} cm^{-1}: 1645 (NC=O). ^1H NMR (100 MHz) δ: 7.96 (1H, s, 11-H), 7.85 (1H, d, *J* 9 Hz, 10-H), 7.56 (1H, s, 4-H), 7.51 (1H, d, *J* 9 Hz, 9-H), 7.48—7.15 (6H, m, aromatic H's), 6.10 (2H, s, 2,3-OCH_2O-), 4.05 (3H, s, 7-OMe), 3.97 (3H, s, 8-OMe), 3.89 (3H, s, 5-Me), 2.08 (3H, s, 12-NPhCOMe). MS Calcd for $C_{29}H_{24}N_2O_6$: M, 496.163. Found *m/z*: M^+, 496.163.

4-Formyl-7,8-dimethoxy-2-methyl-3-4',5'-methylenedioxy-2'-phenyliminomethylphenylisocarbostyril (21)——DDQ (9.6 mg) was added to a solution of **19** (20.0 mg) in benzene (3 ml), and the mixture was refluxed for 1.5 h. Work-up of the reaction mixture gave an oil (19.1 mg), which was purified by prep. TLC (chloroform/ethyl acetate=2/1, v/v) to yield **21** (16.2 mg, 81%), *Rf* 0.33, as colorless prisms of mp 233—234°C (from ethanol). IR ν_{max} cm^{-1}: 1680 (C=O), 1655 (NC=O). ^1H NMR (90 MHz) δ: 9.54 (1H, s, 4-CHO), 8.96 (1H, d, *J* 9 Hz, 5-H), 8.13 (1H, s, 2'-CH=NPh), 7.74 (1H, s, 3'-H), 7.40 (1H, d, *J* 9 Hz, 6-H), 7.27—7.12 (3H, m, aromatic H's), 6.98—6.84 (2H, m, aromatic H's), 6.79 (1H, s, 6'-H), 6.15 (2H, s, 4',5'-OCH_2O-), 3.97 (3H,

s, 8-OMe), 3.94 (3H, s, 7-OMe), 3.28 (3H, s, 2-Me). MS Calcd for $C_{27}H_{22}N_2O_6$: M, 470.148. Found *m/z*: M^+, 470.151.

4-Formyl-3-2′-formyl-4′,5′-methylenedioxyphenyl-7,8-dimethoxy-2-methylisocarbostyril (22)——A solution of **21** (8.4 mg) in methanol (2 ml) containing 10% HCl (1 drop) was stirred at room temperature for 1 h. Work-up of the reaction mixture and prep. TLC (benzene/ethyl acetate=1/1, v/v) gave **22** (6.7 mg, 95%), *Rf* 0.22, as light yellow granules of mp 176—177.5°C (from chloroform/ether). IR ν_{max} cm^{-1}: 1695 (C=O), 1658 (NC=O). ^1H NMR (90 MHz) δ 9.74, 9.43 (1H each, s, 4- and 2′-CHO′s), 8.98 (1H, d, *J* 9 Hz, 5-H), 7.48 (1H, s, 3′-H), 7.40 (1H, d, *J* 9 Hz, 6-H), 6.84 (1H, s, 6′-H), 6.20 (2H, s, 4′,5′-OCH_2O–), 3.98 (3H, s, 8-OMe), 3.96 (3H, s, 7-OMe), 3.21 (3H, s, 2-Me). MS Calcd for $C_{21}H_{17}NO_7$: M, 395.101. Found *m/z*: M^+, 395.101.

5,6-Dihydrochelerythrine (23) and 5,6-Dihydro-7-demethoxychelerythrine (24)——A mixture of $LiAlH_4$ (56.5 mg) and $AlCl_3$ (60.0 mg) in anhydrous 1,2-dimethoxyethane (3 ml) was stirred at room temperature under N_2 for 1 h, and then a solution of **16** (11.3 mg) in anhydrous 1,2-dimethoxyethane (1 ml) was added. The mixture was stirred at room temperature under N_2 for 40 min. Work-up of the reaction mixture gave an oil (6.0 mg), which was purified by prep. TLC (benzene) to yield **23** (2.4 mg, 35%), *Rf* 0.17, and **24** (2.0 mg, 32%), *Rf* 0.36.

5,6-Dihydrochelerythrine (**23**): Colorless prisms of mp 168—170°C (from ethanol). ^1H NMR (90 MHz) δ: 7.69 (1H, d, *J* 9 Hz, 11-H), 7.68 (1H, s, 4-H), 7.51 (1H, d, *J* 8 Hz, 10-H), 7.48 (1H, d, *J* 9 Hz, 12-H), 7.10 (1H, s, 1-H), 6.94 (1H, d, 8 Hz, 9-H), 6.03 (2H, s, 2,3-OCH_2O–), 4.28 (2H, s, 6-H_2), 3.91 (3H, s, 7-OMe), 3.86 (3H, s, 8-OMe), 2.58 (3H, s, 5-Me). MS Calcd for $C_{21}H_{19}NO_4$: M, 349.131. Found *m/z*: M^+, 349.132.

5,6-Dihydro-7-demethoxychelerythrine (**24**): Light yellow prisms of mp 133—135°C (from ethanol). ^1H NMR (90 MHz) δ: 7.71 (2H, d, *J* 8 Hz, 10- and 11-H′s), 7.67 (1H, s, 4-H), 7.48 (1H, d, *J* 8 Hz, 12-H), 7.10 (1H, s, 1-H), 6.93 (1H, dd, *J* 8 and 3 Hz, 9-H), 6.82 (1H, d, *J* 3 Hz, 7-H), 6.03 (2H, s, 2,3-OCH_2O–), 4.15 (2H, s, 6-H_2), 3.85 (3H, s, 8-OMe), 2.58 (3H, s, 5-Me). MS Calcd for $C_{20}H_{17}NO_3$: M, 319.121. Found *m/z*: M^+, 319.122.

The Quinone (5) from the Imine (3) and Diacetoxy Imine (16)——*a*) A solution of **3** (78.6 mg) in methanol (4 ml) containing 10% HCl (0.1 ml) was stirred at room temperature for 30 min. The precipitate was collected and washed with methanol to yield **5** (50.6 mg, 77%) as violet granules of mp 279—280°C.

b) A suspension of **16** (53.0 mg) in 10% HCl (2 ml) was stirred at 80°C for 1.5 h. The precipitate was dissolved in chloroform, and work-up gave **5** (25.2 mg, 69%) as violet granules of mp 278.5—279.5°C.

***cis*-11,12-Dihydro-11,12-dihydroxyoxychelerythrine (25), the *trans* Isomer (26), *cis*-11,12-Diacetoxy-11,12-dihydrooxychelerythrine (27) and the *trans* Isomer (28)**——$NaBH_4$ (20.0 mg) was added to a solution of **5** (41.5 mg) in ethanol (15 ml), and the mixture was stirred at −5°C for 3 h. Work-up of the reaction mixture gave an oil (36.7 mg), which was purified by prep. TLC (chloroform/methanol=50/1, v/v) to yield **25** (7.3 mg, 17%), *Rf* 0.33, and **26** (8.0 mg, 19%), *Rf* 0.28. Unreacted **5** (12.5 mg, 30%) was recovered from the zone with *Rf* 0.67.

Acetylation of **25** and **26** with acetic anhydride/anhydrous pyridine gave the corresponding diacetates (**27**) and (**28**) in 84 and 99% yields, respectively.

The *cis*-Diol (**25**): Colorless granules of mp 282—285°C. This compound was not recrystallized because of its insolubility in solvents. MS Calcd for $C_{21}H_{19}NO_7$: M, 397.116. Found *m/z*: M^+, 397.115.

The *trans*-Diol (**26**): Colorless granules of mp 273—276°C. This compound was not recrystallized because of its insolubility in solvents. MS Calcd for $C_{21}H_{19}NO_7$: M, 397.116. Found *m/z*: M^+, 397.115.

The *cis*-Diacetate (**27**): Light yellow prisms of mp 208—210°C (from ethanol). IR ν_{max} cm^{-1}: 1750 (OC=O), 1645 (NC=O). ^1H NMR (90 MHz) δ: 7.37 (1H, d, *J* 9 Hz, 10-H), 7.28 (1H, d, *J* 9 Hz, 9-H), 6.99 (1H, s, 4-H), 6.93 (1H, d, *J* 1.5 Hz, 1-H), 6.56 (1H, d, *J* 4 Hz, 11-H), 6.13 (1H, dd, *J* 4 and 1.5 Hz, 12-H), 6.03 (2H, s, 2,3-OCH_2O–), 3.99 (3H, s, 7-OMe), 3.92 (3H, s, 8-OMe), 3.68 (3H, s, 5-Me), 2.23 (3H, s, 12-OCOMe), 1.91 (3H, s, 11-OCOMe). Decoupling: δ 6.93 (1-H)→δ 6.13 (dd→d, *J* 4 Hz, 12-H); δ 6.56 (11-H)→δ 6.13 (dd→d, *J* 1.5 Hz, 12-H); δ 6.13 (12-H)→δ 6.93 (d→s, 1-H), 6.56 (d→s, 11-H). NOE: δ 7.35 (10-H)→δ 6.58 (22%, 11-H); δ 6.93 (1-H)→δ 6.13 (9%, 12-H); δ 6.56 (11-H)→δ 7.35 (16%, 10-H); δ 6.13 (12-H)→δ 6.93 (9%, 1-H). MS Calcd for $C_{25}H_{23}NO_9$: M, 481.137. Found *m/z*: M^+, 481.137.

The *trans*-Diacetate (**28**): Light yellow prisms of mp 164—165°C (from ethanol). IR ν_{max} cm^{-1}: 1746 (OC=O), 1643 (NC=O). ^1H NMR (90 MHz) δ: 7.38 (1H, d, *J* 9 Hz, 10-H), 7.29 (1H, d, *J* 9 Hz, 9-H), 7.07 (1H, s, 1-H), 7.00 (1H, s, 4-H), 6.34 (1H, d, *J* 3 Hz, 11-H), 6.02 (2H, s, 2,4-OCH_2O–), 5.68 (1H, d, *J* 3 Hz, 12-H), 3.98 (3H, s, 7-OMe), 3.91 (3H, s, 8-OMe), 3.69 (3H, s, 5-Me), 1.98 (3H, s, 12-OCOMe), 1.93 (3H, s, 11-OCOMe). NOE: δ 7.38 (10-H)—δ 6.34 (21%, 11-H); δ 7.07 (1-H)—δ 5.68 (21%, 12-H); δ 6.34 (11-H)—δ 7.38 (15%, 10-H); δ 5.68 (12-H)—δ 7.07 (20%, 1-H). MS Calcd for $C_{25}H_{23}NO_9$: M, 481.137. Found *m/z*: M^+, 481.136.

12-Methoxyoxychelerythrine (29)——A solution of **26** (4.6 mg) in methanol (4 ml) containing conc. HCl (1 drop) was stirred at room temperature for 1.5 h. Work-up of the reaction mixture gave colorless crystals (4.4 mg), which were methylated with an excess of ethereal diazomethane to yield **29** (4.5 mg, 99%) as colorless needles of mp 108—110°C (from ethanol). IR ν_{max} cm^{-1}: 1637 (NC=O). ^1H NMR (90 MHz) δ: 7.89 (1H, d, *J* 9 Hz, 10-H), 7.62 (1H, s, 11-H), 7.49 (1H, s, 4-H), 7.36 (1H, d, *J* 9 Hz, 9-H), 7.28 (1H, s, 1-H), 6.07 (2H, s, 2,3-OCH_2O–), 4.05 (6H, s, 7- and 12-OMe′s), 3.96 (3H, s, 8-OMe), 3.84 (3H, s, 5-Me). MS Calcd for $C_{22}H_{19}NO_6$: M, 393.121. Found *m/z*: M^+, 393.121.

12-Acetoxyoxychelerythrine (30)——a) A mixture of **28** (17.0 mg) and 10% Pd-C (5.3 mg) in *p*-cymene (0.5 ml) was stirred at 160—165°C for 1 h. Work-up of the reaction mixture gave an oil (9.9 mg), which was purified by prep. TLC (chloroform/ethyl acetate=2/1, v/v) to yield **30** (8.5 mg, 57%), *Rf* 0.38, as colorless needles of mp 213—215°C (from ethanol). IR ν_{max} cm^{-1}: 1765 (OC=O), 1643 (NC=O). ^1H NMR (90 MHz) δ: 7.82 (1H, d, *J* 9 Hz, 10-H), 7.73 (1H, s, 11-H), 7.52 (1H, s, 4-H), 7.33 (1H, d, *J* 9 Hz, 9-H), 7.13 (1H, s, 1-H, 6.07 (2H, s, 2,3-OCH_2O–), 4.05 (3H, s, 7-OMe), 3.94 (3H, s, 8-OMe), 3.84 (3H, s, 5-Me), 2.45 (3H, s, 12-OCOMe). MS Calcd for $C_{23}H_{19}NO_7$: M, 421.116. Found *m/z*: M^+, 421.115.

b) A solution of **28** (10.1 mg) in methanol (1 ml) containing 10% HCl (1 drop) was stirred at room temperature for 19 h. Work-up of the reaction mixture gave **30** (7.5 mg, 85%) as colorless needles of mp 213—215°C (from ethanol).

4bβ,5,6,10b,11,12-Hexahydro-10bβ,12β-(*N*-phenylepoxyimino)chelerythrine (31) and the 4bαH Isomer (32)——$LiAlH_4$ (38.0 mg) was added to a solution of **8** (116.2 mg) in anhydrous 1,2-dimethoxyethane (10 ml), and the mixture was stirred at room temperature under N_2 for 2 h. Work-up of the reaction mixture gave an oil (106.0 mg), which was purified by prep. TLC (acetone/benzene=1/10, v/v) to yield **31** (36.9 mg, 35%), *Rf* 0.29, and **32** (19.2 mg, 18%), *Rf* 0.24.

The 4bβ*H*-10bβ,12β-Epoxyimine (**31**): Colorless prisms of mp 198.5—200°C (from ethanol). IR ν_{max} cm^{-1} ($c=1.11\times10^{-3}$ mol/l): 2768 ($\varepsilon=57$) (Bohlmann band). ^1H NMR (90 MHz) δ: 7.43 (1H, d, *J* 9 Hz, 10-H), 7.18—6.90 (6H, m, aromatic H's), 6.90 (1H, d, *J* 9 Hz, 9-H), 6.65 (1H, s, 1-H), 5.92, 5.87 (1H each, d, *J* 1.5 Hz, 2,3-OCH_2O–), 4.89 (1H, t, *J* 2.5 Hz, 12-H), 4.18 (2H, s, 6-H_2), 4.12 (1H, s, 4b-H), 3.86 (3H, s, 7-OMe), 3.82 (3H, s, 8-OMe), 2.48 (2H, d, *J* 2.5 Hz, 11-H), 2.24 (3H, s, 5-Me). ^{13}C NMR δ: 152.3 (s, C-8), 151.1, 148.0 (s each, C-2 and -3), 147.1 (s, C-1′), 145.7 (s, C-7), 131.5, 131.0 (s each, C-10a and -12a), 129.0 (d, C-3′ and -5′), 128.6, 128.5 (s each, C-4a and -6a), 123.7 (d, C-4′), 122.0 (d, C-10), 116.3 (d, C-2′ and -6′), 111.6 (d, C-4), 110.4 (d, C-1), 107.7 (d, C-9), 101.3 (t, 2,3-OCH_2O–), 80.2 (s, C-10b), 67.0 (d, C-12), 66.0 (d, C-4b), 60.4 (q, 7-OMe), 55.9 (q, 8-OMe), 52.5 (t, C-6), 41.8 (t, C-11), 37.4 (q, 5-Me). MS Calcd for $C_{27}H_{26}N_2O_5$: M, 458.184. Found: *m/z*: M^+, 458.184.

The 4bα*H* Isomer (**32**): Colorless prisms of mp 203.5—205°C (from ethanol). IR ν_{max} cm^{-1} ($c=1.11\times10^{-3}$ mol/l): 2768 ($\varepsilon=30$) (Bohlmann band). ^1H NMR (90 MHz) δ: 7.30 (1H, d, *J* 9 Hz, 10-H), 7.18—6.90 (6H, m, aromatic H's), 6.89 (1H, d, *J* 9 Hz, 9-H), 6.77 (1H, s, 1-H), 5.92 (2H, s, 2,3-OCH_2O–), 4.87 (1H, d, *J* 4 Hz, 12-H), 4.26 (3H, s, 4b-H and 6-H_2), 3.88 (3H, s, 7-OMe), 3.84 (3H, s, 8-OMe), 2.85 (1H, dd, *J* 12 and 4 Hz, 11-H), 2.54 (3H, s, 5-Me), 2.34 (1H, d, *J* 12 Hz, 11-H). ^{13}C NMR δ: 153.3 (s, C-8), 152.1, 149.1 (s each, C-2 and -3), 147.5 (s, C-1′), 146.9 (s, C-7), 130.4, 130.0 (s each, C-10a and -12a), 129.0 (d, C-3′ and -5′), 128.7 (s, C-6a), 126.7 (s, C-4a), 123.4 (d, C-4′), 122.2 (d, C-10), 116.4 (d, C-2′ and -6′), 111.3 (d, C-1), 108.4, 108.0 (d each, C-4 and -9), 101.3 (t, 2,3-OCH_2O–), 80.6 (s, C-10b), 68.1 (d, C-4b), 67.4 (d, C-12), 60.4 (q, 7-OMe) 56.0 (q, 8-OMe), 52.3 (t, C-6), 41.1 (t, C-11), 37.2 (q, 5-Me). MS Calcd for $C_{27}H_{26}N_2O_5$: M, 458.184. Found *m/z*: M^+, 458.185.

12β-Anilino-4bβ,5,6,10b,11,12-hexahydro-10bβ-hydroxychelerythrine (33)——A solution of **31** (26.9 mg) in methanol (20 ml) was shaken with H_2 over 10% Pd-C (6.0 mg) at room temperature for 3 h. The reaction mixture was filtered and concentrated *in vacuo*. The residual oil (25.7 mg) was purified by prep. TLC (acetone/benzene=1/10, v/v) to yield **33** (15.2 mg, 56%), *Rf* 0.35, as colorless prisms of mp 206—207.5°C (from chloroform/ether). IR ν_{max} cm^{-1} ($c=1.17\times10^{-3}$ mol/l): 3592 ($\varepsilon=69$) (OH···π), 3420 ($\varepsilon=39$) (NH), 3390 ($\varepsilon=40$) (OH···N), 2768 ($\varepsilon=138$) (Bohlmann band). ^1H NMR (90 MHz) δ: 7.21—7.12 (2H, m, aromatic H's), 6.92—6.55 (7H, m, aromatic H's), 5.92 (2H, s, 2,3-OCH_2O–), 4.60 (1H, t, *J* 5 Hz, 12-H), 4.02 (1H, d, *J* 17 Hz, 6-H), 3.82 (4H, s, 7-OMe and 12-NHPh[4]), 3.80 (3H, s, 8-OMe), 3.53 (1H, d, *J* 17 Hz, 6-H), 3.40 (1H, s, 4b-H), 3.02 (1H, s, 10b-OH),[4] 2.79 (1H, dd, *J* 14 and 5 Hz, 11-H), 2.38 (3H, s, 5-Me), 2.10 (1H, dd, *J* 14 and 5 Hz, 11-H). ^{13}C NMR δ: 152.3 (s, C-8), 151.1, 148.0 (s each, C-2 and -3), 147.1 (s, C-1′), 145.7 (s, C-7), 131.5, 131.0 (s each, C-10a and -12a), 129.0 (d, C-3′ and -5′), 128.6, 128.5 (s each, C-4a and -6a), 123.7 (d, C-4′), 122.0 (d, C-10), 116.3 (d, C-2′ and -6′), 111.6 (d, C-4), 110.4 (d, C-1), 107.9 (d, C-9), 101.3 (t, 2,3-OCH_2O–), 80.2 (s, C-10b), 67.0 (d, C-12), 66.0 (d, C-4b), 60.4 (q, 7-OMe), 55.9 (q, 8-OMe), 52.5 (t, C-6), 41.8 (t, C-11), 37.4 (q, 5-Me). MS Calcd for $C_{27}H_{28}N_2O_5$: M, 460.200. Found *m/z*: M^+, 460.199.

Unreacted **31** (1.7 mg, 6%) was recovered from the zone with *Rf* 0.49.

12β-Anilino-4bα,5,6,10b,11,12-hexahydro-10bβ-hydroxychelerythrine (34)——A solution of **32** (21.3 mg) in methanol (20 ml) was shaken with H_2 over 10% Pd-C (6.0 mg) at room temperature for 20 h. Work-up of the reaction mixture gave an oil (22.3 mg), which was purified by prep. TLC (acetone/benzene=1/10, v/v) to yield **34** (14.7 mg, 69%), *Rf* 0.35, as colorless prisms of mp 132.5—133.5°C (from ethanol). IR ν_{max} cm^{-1} ($c=1.30\times10^{-3}$ mol/l): 3620 ($\varepsilon=44$) (OH), 3420 ($\varepsilon=44$) (NH), 3395 ($\varepsilon=52$) (OH···N), 2768 ($\varepsilon=54$) (Bohlmann band). ^1H NMR (90 MHz) δ: 7.29 (1H, s, 4-H), 7.25—7.17 (2H, m, aromatic H's), 6.94—6.70 (6H, m, aromatic H's), 5.93 (2H, s, 2,3-OCH_2O–), 4.73 (1H, d, *J* 6 Hz, 12-H), 4.31 (1H, d, *J* 17 Hz, 6-H), 4.20 (1H, s, 4b-H), 4.13 (1H, s, 12-NHPh),[4] 3.90 (1H, d, *J* 17 Hz, 6-H), 3.83 (3H, s, 7-OMe), 3.81 (3H, s, 8-OMe), 2.81 (1H, d, *J* 14 Hz, 11-H), 2.55 (3H, s, 5-Me), 2.22 (1H, s, 10b-OH),[4] 1.98 (1H, dd, *J* 14 and 6 Hz, 11-H). ^{13}C NMR δ: 153.3 (s, C-8), 152.1, 149.1 (s each, C-2 and -3), 147.5 (s, C-1′), 146.9 (s, C-7), 130.4, 130.0 (s each, C-10a and -12a), 129.0 (d, C-3′ and -5′), 128.7 (s, C-6a), 126.7 (s, C-4a), 123.4 (d, C-4′), 122.2 (d, C-10), 116.4 (d, C-2′ and -6′), 111.3 (d, C-1), 108.4, 108.0 (d each, C-4 and -9), 101.3 (t, 2,3-OCH_2O–), 80.6 (s, C-10b), 68.1 (d, C-4b), 67.4 (t, C-12), 60.4 (q, 7-OMe), 56.0 (q, 8-OMe), 53.2 (t, C-6), 41.1 (t, C-11), 37.2 (q, 5-Me).

MS Calcd for $C_{27}H_{28}N_2O_5$: M, 460.200. Found *m/z*: M^+, 460.199.
Unreacted **32** (1.7 mg, 8%) was recovered from the zone with *Rf* 0.44.

References and Notes

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