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Synthesis of the Erythrinan Skeleton by Acid-Promoted Cyclization of *N*-(3-Oxo-1-cyclohexen-1-yl)-*N*-[2-(3,4-dimethoxyphenyl)ethyl]-α-(methylsulfinyl)acetamide

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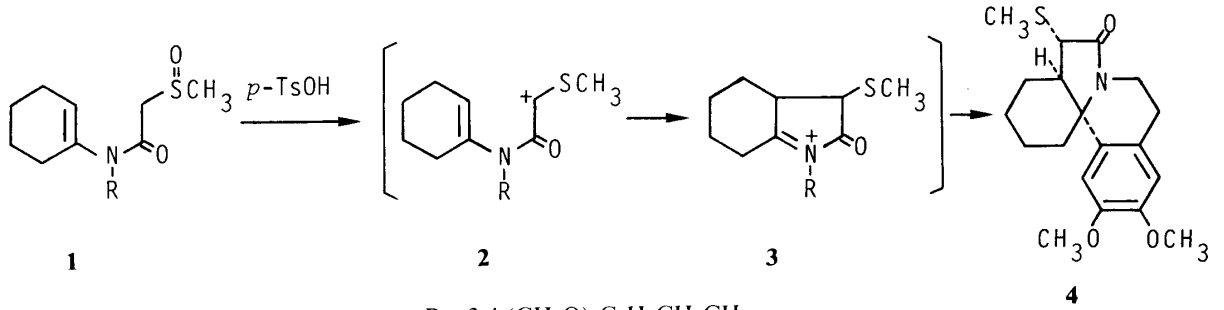
Heating of the *N*-(3-oxo-1-cyclohexene-1-yl)-α-(methylsulfinyl)acetamides **7a**—**c** with *p*-toluenesulfonic acid in 1,2-dichloroethane gave the 3,5,6,7-tetrahydro-3-methylthio-1*H*-indole-2,4-diones **9a**—**c**. Compound **9b**, when heated in 85% phosphoric acid at 80 °C, underwent further cyclization to afford the 7-(methylthio)erythrinan-1,8-dione **14** and the 6,7-didehydroerythrinan-1,8-dione **15** in 53 and 15% yields, respectively. Refluxing of **9b** in 99% formic acid gave **15** in 43% yield. Double cyclization of **7b** to **14** and **15** was achieved by refluxing in 99% formic acid in 7 and 47% yields, respectively. In marked contrast, treatment of **9c** with formic acid resulted in the formation of the 1,3-dihydro-4-hydroxy-2-methylthio-2*H*-indol-2-one **16** and the 3,5,6,7-tetrahydro-1*H*-indole-2,4-dione **17** in 47 and 16% yields, respectively.

Keywords——erythrinan-1,8-dione; 6,7-didehydroerythran-1,8-dione; enaminoketone; Pummerer reaction; phosphoric acid; formic acid; oxindole

In previous papers,[1] we reported that the treatment of *N*-(1-cyclohexen-1-yl)-*N*-[2-(3,4-dimethoxyphenyl)ethyl]-α-(methylsulfinyl)acetamide (**1**) with *p*-toluenesulfonic acid provided a one step synthesis of the erythrinan skeleton **4** through cyclization of the thionium ion **2** and successive cyclization of the resultant *N*-acyliminium ion **3**.



1 **2** **3** **4**

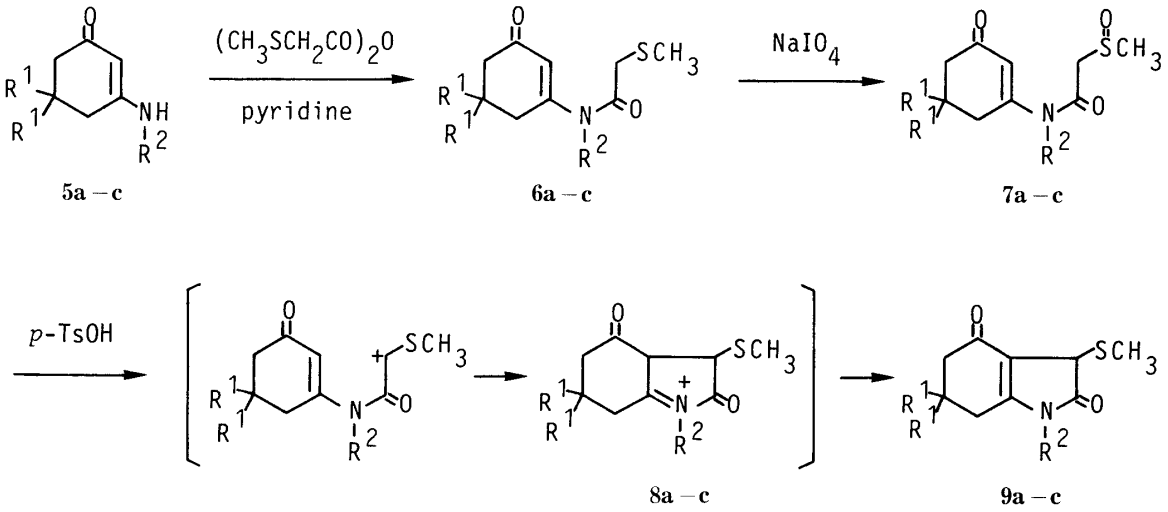
R = 3,4-$(CH_3O)_2C_6H_3CH_2CH_2$–

Chart 1

Our attention has now been drawn to the enaminoketone system **7**, which might afford a new route to erythrinan-1,8-dione and homoerythrinan-1,8-dione, potential intermediates in the total synthesis of the *Erythrina* alkaloids. The starting sulfoxides **7a**—**c** were prepared by *N*-acylation of the corresponding enaminoketones **5a**—**c** with α-(methylthio)acetic anhydride and pyridine followed by oxidation of the resultant *N*-[α-(methylthio)acetyl]enaminoketones

6a—**c** with sodium metaperiodate.

Treatment of **7a** with *p*-toluenesulfonic acid in boiling 1,2-dichloroethene was found to give 3,5,6,7-tetrahydro-6,6-dimethyl-3-methylthio-1-phenyl-1*H*-indole-2,4-dione (**9a**) in 64% yield, whose structure was confirmed by the spectroscopic evidence (Experimental). Being encouraged by this preliminary experiment, we next treated the sulfoxides **7b** and **7c** in a similar manner in an attempt to achieve double cyclization to the erythrinan and homoerythrinan skeletons. However, these sulfoxides **7b**, **c** gave only the bicyclic products **9b** and **9c** in 75 and 84% yields, respectively. Deprotonation from the *N*-acyliminium ion intermediates **8b** and **8c** to form the highly stabilized enaminoketone systems **9b** and **9c** appears to be kinetically favored over the intramolecular attack of an aromatic ring on the cations **8b** and **8c**.



5a—**c** **6a**—**c** **7a**—**c**

8a—**c** **9a**—**c**

a: $R^1=CH_3$, $R^2=C_6H_5$
b: $R^1=H$, $R^2=3,4\text{-}(CH_3O)_2C_6H_3CH_2CH_2-$
c: $R^1=H$, $R^2=3,4\text{-}(CH_3O)_2C_6H_3CH_2CH_2CH_2-$

Chart 2

A survey of the literature revealed that phosphoric acid[2] or formic acid[3] promotes the cyclization of the *N*-acyl-enaminoketones **10** and **11**, giving the erythrinans **12** and **13**, respectively. Thus, when **9b** was allowed to react with 85% phosphoric acid at 80 °C for 2 h, the expected erythrinan derivative **14** was obtained in 53% yield together with **15** (15%). Heating of **9b** in refluxing 99% formic acid gave **15** (43%) as a major product, along with a trace amount of **14**. The structures of **14** and **15** were deduced from the following spectroscopic data. The infrared (IR) spectrum ($CHCl_3$) of **14** showed a single carbonyl absorption at 1690 cm^{-1}. The ^1H-nuclear magnetic resonance (NMR) spectrum of **14** showed three methyl singlets at δ 2.08 (SMe), 3.83, and 3.85 (OMe), two doublets at δ 3.00 (1H, H-6, $J=9$ Hz) and 3.79 (1H, H-7, $J=9$ Hz), and two singlets at δ 6.38 and 6.54 (1H each, H-14 and 17). The *cis*-stereochemistry of the A/B ring junction of **14** was confirmed by transforming it to the known erythrinan **12** by desulfurization with Raney nickel. The stereochemistry of the methylthio group was tentatively assigned as α by comparison of the coupling constant (9 Hz) between H-6 and H-7 with that (10 Hz) of **4**.[1] The IR spectrum of **15** showed strong absorptions at 1680 (C=O) and 1615 (C=C) cm^{-1}. The ^1H-NMR spectrum clearly indicated the absence of the methylthio group and instead the presence of one olefinic proton at δ 6.25 (1H, s). The formation of **15** is considered to proceed by acid-catalyzed elimination of methyl mercaptan from **14**. In fact, compound **15** was formed by refluxing **14** in formic acid.

Phosphoric acid or formic acid may also act as an activator for the Pummerer reaction of

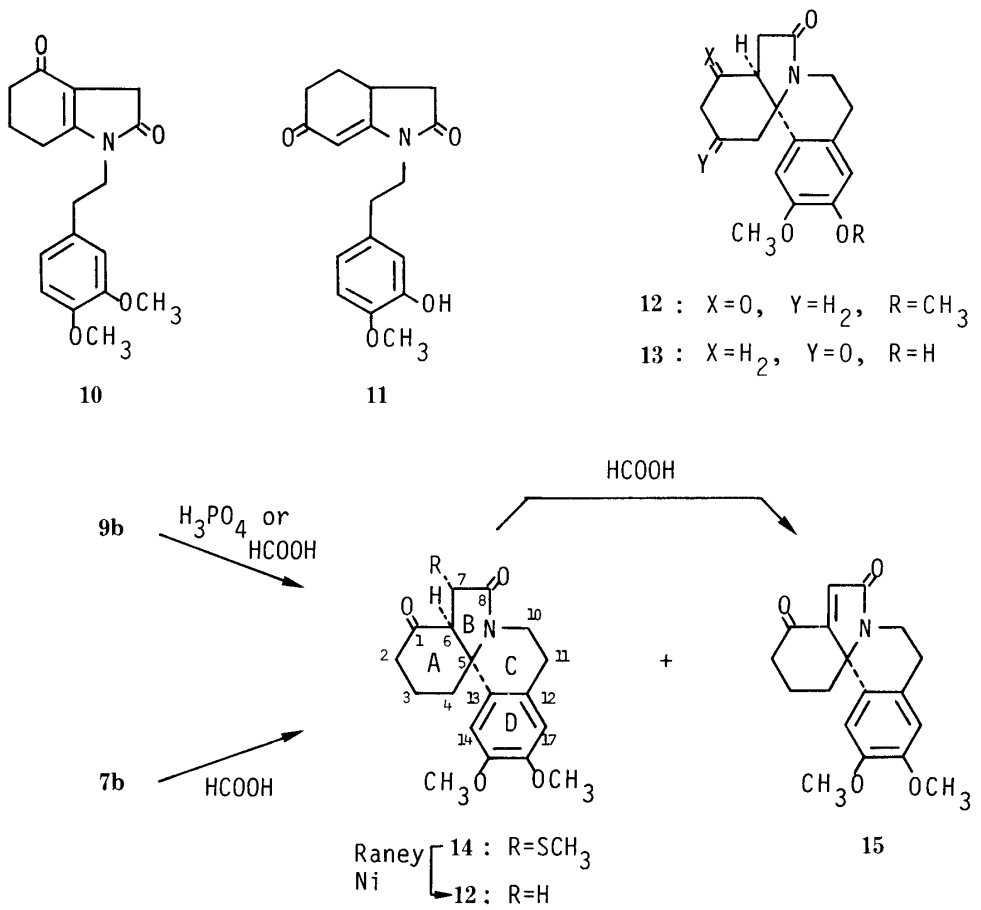


Chart 3

α-acylsulfoxides. This consideration led us to examine the possibility of the double cyclization of the sulfoxide **7b** into the erythrinan skeleton. An initial attempt to cyclize **7b** by heating with 85% phosphoric acid at 80 °C gave an equivocal result. However, refluxing of **7b** in 99% formic acid directly furnished the desired erythrinan derivatives **14** (7%) and **15** (47%).

In marked contrast to the case of **9b**, refluxing of **9c** in 99% formic acid afforded only the aromatized product **16** (47%) and the reduction product **17** (16%), but none of the expected cyclization product **18**.

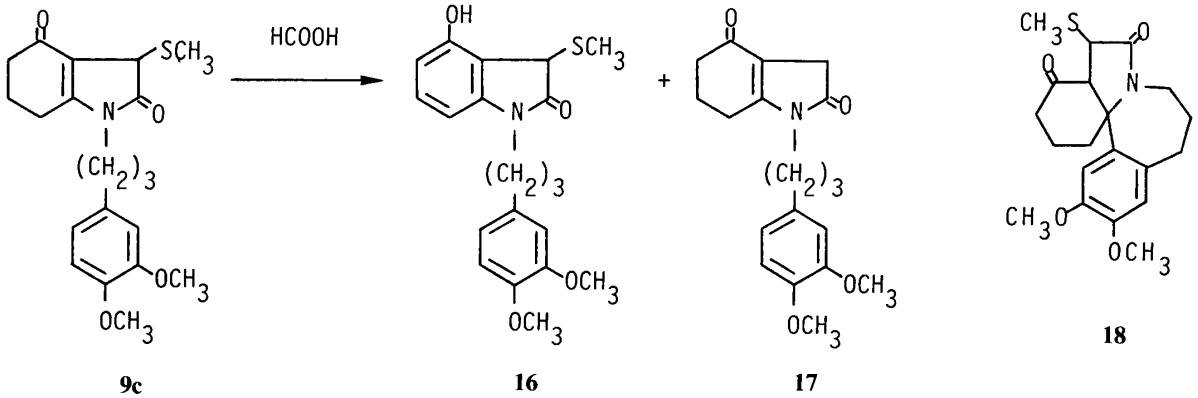


Chart 4

The total synthesis of some naturally occurring *Erythrina* alkaloids, based on the present sequence of reactions, is currently under way.

Experimental

IR spectra were recorded with a JASCO-IRA-1 or A-100 spectrophotometer. ^{1}H-NMR spectra were determined with a Hitachi R-22 (90 MHz) or JEOL JNM-PMX 60 (60 MHz) spectrometer, and δ values are quoted relative to tetramethylsilane. High-resolution mass spectra (MS) were obtained on a Hitachi M-80 instrument at 20 eV. Chromatographic separation was performed with Silica gel 60 (70—230 mesh) (Merck).

3-[3-(3,4-Dimethoxyphenyl)propylamino]-2-cyclohexen-1-one (5c)——A solution of 3-(3,4-dimethoxyphenyl)-propylamine[4] (996 mg, 5.1 mmol) and cyclohexane-1,3-dione (686 mg, 6.1 mmol) in benzene (50 ml) was refluxed in a flask equipped with a water separator for 2 h. After removal of the solvent, the residue was dissolved in $CHCl_3$ (30 ml); the solution was washed with saturated $NaHCO_3$ solution, and dried ($MgSO_4$). The solvent was removed by evaporation and the residue was chromatographed on silica gel (acetone) to give **5c** (1.43 g, 97%), mp 111—111.5 °C (from benzene). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3220, 1600, 1550, 1510. ^{1}H-NMR ($CDCl_3$) δ: 1.7—2.4 (8H, m, H-4, 5, 6, $NCH_2C\underline{H}_2$), 2.63 (2H, t, J=7 Hz, $ArC\underline{H}_2$), 3.10 (2H, q, J=7 Hz, NCH_2), 3.81 (6H, s, 2×OMe), 4.5—4.9 (1H, br, NH), 5.04 (1H, s, H-2), 6.6—6.7 (3H, m, arom.). *Anal.* Calcd for $C_{17}H_{23}NO_3$: C, 70.56; H, 8.01; N, 4.84. Found: C, 70.86; H, 7.83; N, 5.16.

***N*-(5,5-Dimethyl-3-oxo-1-cyclohexen-1-yl)-*N*-phenyl-α-(methylthio)acetamide (6a)**——A solution of **5a**[5] (2.78 g, 12.9 mmol) in α-(methylthio)acetic anhydride[6] (12.8 g, 66 mmol) and pyridine (0.5 ml, 6.3 mmol) was heated at 160 °C for 1 h. After removal of the solvent *in vacuo*, $CHCl_3$ (50 ml) and 10% HCl solution (200 ml) were added to the residue and the mixture was stirred vigorously at room temperature for 10 h. The organic layer was separated and the aqueous layer was further extracted with $CHCl_3$. The combined organic layers were washed with saturated $NaHCO_3$ solution and brine, then dried ($MgSO_4$). The solvent was evaporated off and the residue was chromatographed on silica gel (benzene–ethyl acetate, 5 : 1) to give **6a** (2.1 g, 54%) as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650. ^{1}H-NMR ($CDCl_3$) δ: 1.09 (6H, s, CMe_2), 2.20 (3H, s, SMe), 2.24 (2H, s, H-6), 2.72 (2H, br s, H-4), 3.05 (2H, s, SCH_2), 5.40 (1H, br s, H-2), 7.05—7.55 (5H, m, arom.). *Anal.* Calcd for $C_{17}H_{21}NO_2S$: C, 67.30; H, 6.98; N, 4.62. Found: C, 67.03; H, 6.97; N, 4.38.

***N*-[2-(3,4-Dimethoxyphenyl)ethyl]-*N*-(3-oxo-1-cyclohexen-1-yl)-α-(methylthio)acetamide (6b)**——By a procedure similar to that described above for the preparation of **6a**, except that the reaction temperature was raised to 70—80 °C, compound **6b** (4.30 g, 60%) was obtained from **5b**[2] (5.44 g, 19.8 mmol), α-(methylthio)acetic anhydride (16.6 g, 86 mmol), and pyridine (0.6 ml, 7.6 mmol) as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650, 1620. ^{1}H-NMR ($CDCl_3$) δ: 1.9—3.0 (8H, m, H-4, 5, 6, $ArC\underline{H}_2$), 2.19 (3H, s, SMe), 3.27 (2H, s, SCH_2), 3.6—4.1 (2H, m, NCH_2); 3.84 (6H, s, 2×OMe), 5.81 (1H, br s, H-2), 6.70 (3H, br s, arom.). *Anal.* Calcd for $C_{19}H_{25}NO_4S$: C, 62.79; H, 6.93; N, 3.85. Found: C, 62.59; H, 6.98; N, 3.68.

***N*-[3-(3,4-Dimethoxyphenyl)propyl]-*N*-(3-oxo-1-cyclohexen-1-yl)-α-(methylthio)acetamide (6c)**——By a procedure similar to that described above for the preparation of **6b**, compound **6c** (1.02 g, 57%) was obtained from **5c** (1.37 g, 5 mmol), α-(methylthio)acetic anhydride (4.85 g, 25 mmol), and pyridine (0.2 ml, 2.6 mmol) as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650, 1620, 1510. ^{1}H-NMR ($CDCl_3$) δ: 1.8—2.7 (10H, m, H-4, 5, 6, $ArC\underline{H}_2C\underline{H}_2$), 2.19 (3H, s, SMe), 3.27 (2H, s, SCH_2), 3.4—4.0 (2H, m, NCH_2), 3.80 (6H, s, 2×OMe), 5.80 (1H, br s, H-2), 6.55—6.70 (3H, m, arom.). Exact MS *m/z*: calcd for $C_{20}H_{27}NO_4S$: 377.1658. Found: 377.1613.

***N*-(5,5-Dimethyl-3-oxo-1-cyclohexen-1-yl)-*N*-phenyl-α-(methylsulfinyl)acetatmide (7a)**——A solution of sodium metaperiodate (1.10 g, 5.1 mmol) in water (10 ml) was added dropwise to an ice-cooled solution of **6a** (1.41 g, 4.65 mmol) in methanol (25 ml), and stirring was continued at room temperature for 10 h. The precipitated inorganic material was removed by filtration and the filtrate was extracted with $CHCl_3$, then the organic layer was dried ($MgSO_4$). The solvent was evaporated off and the residue was chromatographed on silica gel (benzene–ethyl acetate, 1 : 1) to give **7a** (1.29 g, 87%) as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650. ^{1}H-NMR ($CDCl_3$) δ: 1.05 (6H, s, CMe_2), 2.22 (2H, s, H-6), 2.64 (2H, br s, H-4), 2.68 (3H, s, SOMe), 3.60 (2H, s, $SOCH_2$), 5.47 (1H, br s, H-2), 7.05—7.60 (5H, m, arom.). *Anal.* Calcd for $C_{17}H_{21}NO_3S$: C, 63.92; H, 6.63; N, 4.39. Found: C, 63.48; H, 6.74; N, 4.39.

***N*-[2-(3,4-Dimethoxyphenyl)ethyl]-*N*-(3-oxo-1-cyclohexen-1-yl)-α-(methylsulfinyl)acetamide (7b)**——By a procedure similar to that described above for the preparation of **7a**, compound **7b** (2.21 g, 87%) was obtained by oxidation of **6b** (2.43 g, 6.69 mmol) with sodium metaperiodate (1.71 g, 8.0 mmol) as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1655, 1620. ^{1}H-NMR ($CDCl_3$) δ: 1.7—3.0 (8H, m, H-4, 5, 6, $ArC\underline{H}_2$), 2.72 (3H, s, SOMe), 3.55—4.10 (4H, m, $SOCH_2$, NCH_2), 3.82 (3H, s, OMe), 3.84 (3H, s, OMe), 5.80 (1H, s, H-2), 6.74 (3H, br s, arom.). *Anal.* Calcd for $C_{19}H_{25}NO_5S \cdot 1/4H_2O$: C, 59.43; H, 6.69; N, 3.64. Found: C, 59.48; H, 6.69; N, 3.54. Exact MS *m/z*: Calcd for $C_{19}H_{25}NO_5S$: 379.1451. Found: 379.1443.

***N*-[3-(3,4-Dimethoxyphenyl)propyl]-*N*-(3-oxo-1-cyclohexen-1-yl)-α-(methylsulfinyl)acetamide (7c)**——By a procedure similar to that described above for the preparation of **7a**, compound **7c** (758 mg, 72%) was obtained by oxidation of **6c** (1.02 g, 2.8 mmol) with sodium metaperiodate (670 mg, 3.1 mmol) as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1655, 1620, 1515. ^{1}H-NMR ($CDCl_3$) δ: 1.6—2.8 (10H, m, H-4, 5, 6, $ArC\underline{H}_2C\underline{H}_2$), 2.70 (3H, s, SOMe), 3.5—4.0 (4H, m, $SOCH_2$, NCH_2), 3.77 (6H, s, 2×OMe), 5.80 (1H, br s, H-2), 6.65 (3H, br s, arom.). Exact MS *m/z*: Calcd for $C_{20}H_{27}NO_5S$: 393.1608. Found: 393.1630.

3,5,6,7-Tetrahydro-6,6-dimethyl-3-methylthio-1-phenyl-1*H*-indole-2,4-dione (9a)——A solution of **7a** (399 mg,

1.25 mmol) and anhydrous *p*-toluenesulfonic acid (430 mg, 2.50 mmol) in 1,2-dichloroethane (15 ml) was heated under reflux for 15 min. The reaction mixture was washed with saturated $NaHCO_3$ solution and water, and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was chromatographed on silica gel (benzene–ethyl acetate, 1 : 1) to give **9a** (241 mg, 64%), mp 164—165 °C [from benzene–*n*-hexane (2 : 1)]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735, 1640, 1610, 1600. ^{1}H-NMR ($CDCl_3$) δ: 1.10 (6H, s, CMe_2), 2.3—2.4 (4H, m, H-4, 6), 2.31 (3H, s, SMe), 4.18 (1H, t, J = 2 Hz, H-3), 7.05—7.60 (5H, m, arom.). *Anal.* Calcd for $C_{17}H_{19}NO_2S$: C, 67.75; H, 6.35; N, 4.65. Found: C, 67.92; H, 6.39; N, 4.48.

3,5,6,7-Tetrahydro-1-[2-(3,4-dimethoxyphenyl)ethyl]-3-methylthio-1*H*-indole-2,4-dione (9b)——By a procedure similar to that described above for the preparation of **9a**, compound **9b** (682 mg, 75%) was obtained from **7b** (965 mg, 2.5 mmol), mp 139—140 °C (from toluene). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1635, 1605. ^{1}H-NMR ($CDCl_3$) δ: 1.7—2.5 (6H, m, H-4, 5, 6), 2.32 (3H, s, SMe), 2.84 (2H, t, J = 6.5 Hz, $ArC\underline{H}_2$), 3.3—3.9 (2H, m, NCH_2), 3.83 (6H, s, 2 × OMe), 4.00 (1H, br s, H-3), 6.5—6.9 (3H, m, arom.). *Anal.* Calcd for $C_{19}H_{23}NO_4S$: C, 63.14; H, 6.41; N, 3.88. Found: C, 63.12; H, 6.49; N, 3.79.

3,5,6,7-Tetrahydro-1-[3-(3,4-dimethoxyphenyl)propyl]-3-methylthio-1*H*-indole-2,4-dione (9c)——By a procedure similar to that described above for the preparation of **9a**, compound **9c** (120 mg, 84%) was obtained from **7c** (150 mg, 0.38 mmol) as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1640, 1605. ^{1}H-NMR ($CDCl_3$) δ: 1.7—2.9 (8H, m, H-4, 5, 6, $ArCH_2C\underline{H}_2$), 2.26 (3H, s, SMe), 3.3—3.8 (4H, m, $ArC\underline{H}_2$, NCH_2), 3.82 (6H, s, 2 × OMe), 4.00 (1H, br t, J = 2 Hz, H-3), 6.6—6.7 (3H, m, arom.). Exact MS *m/z*: Calcd for $C_{20}H_{25}NO_4S$: 375.1503. Found: 375.1517.

15,16-Dimethoxy-7-methylthio-*cis*-erythrinan-1,8-dione (14) and 6,7-Didehydro-15,16-dimethoxyerythrinan-1,8-dione (15)——a) By Cyclization of **9b** with Phosphoric Acid: A solution of **9b** (190 mg, 0.53 mmol) in 85% phosphoric acid (7 ml) was heated at 80 °C for 2 h. The reaction mixture was poured into $CHCl_3$ (40 ml) and neutralized with 20% NaOH solution. The organic layer was separated and the aqueous layer was further extracted with $CHCl_3$. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated off, then the residue was chromatographed on silica gel (benzene–acetone, 2 : 1). The first eluate gave **14** (100 mg, 53%), mp 202—203 °C (from benzene). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690. ^{1}H-NMR ($CDCl_3$) δ: 1.7—2.3 (4H, m, H-3,4), 2.08 (3H, s, SMe), 2.5—2.9 (4H, m, H-2, 11), 3.00 (1H, d, J = 9 Hz, H-6), 3.1—3.5 (1H, m, H-10), 3.79 (1H, d, J = 9 Hz, H-7), 3.83 (3H, s, OMe), 3.85 (3H, s, OMe), 4.05—4.35 (1H, m, H-10), 6.38 (1H, s, arom.), 6.54 (1H, s, arom.). *Anal.* Calcd for $C_{19}H_{23}NO_4S$: C, 63.14; H, 6.41; N, 3.88. Found: C, 62.89; H, 6.35; N, 3.82. The second eluate gave **15** (25 mg, 15%), mp 162.5—163.5 °C (from *n*-hexane–ethanol). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680, 1615. ^{1}H-NMR ($CDCl_3$): δ: 1.7—3.2 (8H, m, H-2, 3, 4, 11), 3.5—4.1 (2H, m, H-10), 3.73 (3H, s, OMe), 3.83 (3H, s, OMe), 6.25 (1H, s, H-7), 6.36 (1H, s, arom.), 6.67 (1H, s, arom.). *Anal.* Calcd for $C_{18}H_{19}NO_4$: C, 69.00; H, 6.11; N, 4.47. Found: C, 68.85; H, 6.14; N, 4.44.

b) By Cyclization of **9b** with Formic Acid: A solution of **9b** (133 mg, 0.37 mmol) in 99% formic acid (3 ml) was heated under reflux for 20 h. The solvent was removed *in vacuo* and the residue was dissolved in $CHCl_3$ (30 ml). The resultant solution was washed with saturated $NaHCO_3$ solution and dried ($MgSO_4$). The solvent was removed by evaporation and the residue was chromatographed on silica gel (benzene–acetone, 2 : 1) to give **14** (trace) and **15** (50 mg, 43%).

c) By Cyclization of **7b** with Formic Acid: A solution of **7b** (750 mg, 1.97 mmol) in 99% formic acid (20 ml) was heated under reflux for 38 h. The reaction mixture was worked-up by the same procedure as above (**b**) to give **14** (50 mg, 7%) and **15** (288 mg, 47%).

Transformation of 14 into 15——A solution of **14** (8 mg, 0.02 mmol) in 99% formic acid (3 ml) was heated under reflux for 14 h and the solvent was removed *in vacuo*. The crude reaction mixture was shown to contain **15** along with a trace amount of unchanged **14** by ^{1}H-NMR spectroscopy and thin layer chromatography.

15,16-Dimethoxy-*cis*-erythrinan-1,8-dione (12)——Raney nickel (*ca.* 1 g) was added to acetone (10 ml), and the mixture was refluxed for 1 h. After cooling of the mixture, a solution of **14** (80 mg, 0.22 mmol) in acetone (1 ml) was added and the resultant mixture was again refluxed for 6 h. The Raney nickel was removed by filtration, the filtrate was concentrated, and the residue was chromatographed on silica gel (ethyl acetate) to give **12** (35 mg, 44%), mp 156 °C (from ethanol) (lit.[2] 157 °C).

1,3-Dihydro-4-hydroxy-1-[3-(3,4-dimethoxyphenyl)propyl]-2-methylthio-2*H*-indol-2-one (16) and 3,5,6,7-Tetrahydro-1-[3-(3,4-dimethoxyphenyl)propyl]-1*H*-indole-2,4-dione (17)——A solution of **9c** (98 mg, 0.25 mmol) in 99% formic acid (3 ml) was heated at 100 °C for 20 h. After removal of the solvent *in vacuo*, the residue was dissolved in $CHCl_3$ (10 ml) and washed with saturated $NaHCO_3$ solution, then dried ($MgSO_4$). The solvent was evaporated off and the residue was chromatographed on silica gel (ethyl acetate–benzene, 1 : 1). The first eluate gave **16** (43.7 mg, 47%), mp 146—146.5 °C (from ethanol). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1710, 1625. ^{1}H-NMR ($CDCl_3$) δ: 1.7—2.3 (2H, m, $NCH_2C\underline{H}_2$), 1.97 (3H, s, SMe), 2.61 (2H, br t, J = 7 Hz, $ArC\underline{H}_2$), 3.65 (2H, t, J = 7 Hz, NCH_2), 3.79 (6H, s, 2 × OMe), 4.24 (1H, s, H-3), 6.40 (1H, d, J = 7.5 Hz, arom.), 6.70 (1H, d, J = 8 Hz, arom.), 6.7—7.5 (4H, m, arom.). *Anal.* Calcd for $C_{20}H_{23}NO_4S$: C, 64.32; H, 6.21; N, 3.75. Found: C, 63.79; H, 6.13; N, 3.63. The second eluate gave **17** (12.9 mg, 16%) as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725, 1640, 1615. ^{1}H-NMR ($CDCl_3$) δ: 1.7—2.8 (10H, m, H-5, 6, 7, $ArC\underline{H}_2C\underline{H}_2$), 3.17 (2H, br t, J = 2 Hz, H-3), 3.53 (2H, t, J = 7.5 Hz, NCH_2), 3.82 (3H, s, OMe), 3.84 (3H, s, OMe), 6.60—6.75 (3H, m, arom). Exact MS *m/z*: Calcd for $C_{19}H_{23}NO_4$: 329.1627. Found: 329.1621.

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References and Notes

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