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Synthesis of 3-Demethoxyerythratidinone *via* Formation of a Dibenzazonine Alkaloid

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3-Demethoxyerythratidinone (**1**) was synthesized *via* the dibenzazonine base (**7**), which was prepared by irradiation of the phenolic compound (**5**) in an alkaline solution, followed by reduction of the resulting photocyclization product (**6**) with diborane. We investigated various oxidation reactions of **7** to yield the corresponding dienone (**11**). It was found that the use of active lead oxide and potassium ferricyanide as oxidants gave the dienone (**11**) in 65 and 60% yields, respectively. Finally, the dienone (**11**) was converted to **1** by hydrogenation.

Keywords——3-demethoxyerythratidinone; erythrina alkaloid; dibenzazonine alkaloid; photocyclization reaction; phenol oxidation; lead dioxide, potassium ferricyanide

In the course of our investigation of Erythrina alkaloids, we isolated[1] erybidine, which has a dibenzazonine skeleton. The demethyl derivative of erybidine, 5,6,8,9-tetrahydro-2,12-dimethoxy-7*H*-dibenz[*d,f*]azonine-3,11-diol, plays an important role in the biosynthesis of Erythrina alkaloids[2] and can be converted into erysodienone *in vitro*[3] in good yield. Furthermore, Franck *et al.*[4] reported the synthesis of 14-methoxyerysodienone *via* phenol oxidation of a dibenzazonine alkaloid with potassium ferricyanide.

On the other hand, 3-demethoxyerythratidinone (**1**) was isolated from *Erythrina lithosperma* BLUME by Barton *et al.*[5] This alkaloid, which is unique in the *Erythrina* genus in its lack of a 3-methoxy group, might be biosynthesized from the known Erythrina base, erythratidinone.[5]

We wish to describe here a convenient synthesis of 3-demethoxyerythratidinone *via* the dibenzazonine derivative (**7**).

Synthesis

The key intermediate compound (**7**) in the synthesis of 3-demethoxyerythratidinone was prepared as follows. 6-Bromo-3,4-dimethoxyphenylacetic acid (**2**)[6] was heated with 3-benzyloxyphenethylamine (**3**) to produce the corresponding amide (**4**) in an excellent yield. Treatment of **4** with a mixture of conc. hydrochloric acid and ethanol afforded the phenolic compound (**5**) in 88% yield. Irradiation[7] of **5** in methanol in the presence of sodium hydroxide with a 100 W high pressure mercury lamp at room temperature gave the amides (**6**, **8**, and **9**) in 57, 4, and 13% yields, respectively. The structures of these substances (**6**, **8**, and **9**) were assigned on the basis of spectral and chemical studies.

The major product (**6**), mp 297—298 °C, $C_{18}H_{19}NO_4$, displayed the molecular peak at *m/z* 313 as the base peak in the mass spectrum (MS) and its infrared (IR) spectrum revealed the presence of a hydroxyl group (3500 cm^{-1}) and an amide group (3400 and 1650 cm^{-1}). The nuclear magnetic resonance (NMR) spectrum showed five protons (δ 6.45—7.38) as a complex signal in the aromatic proton region and two methoxyl groups (δ 3.73 and 3.78). In order to clarify the aromatic substitution pattern and to obtain the desired secondary amine (**7**), the product (**6**) was reduced with diborane to provide **7** in 93% yield. The NMR spectrum

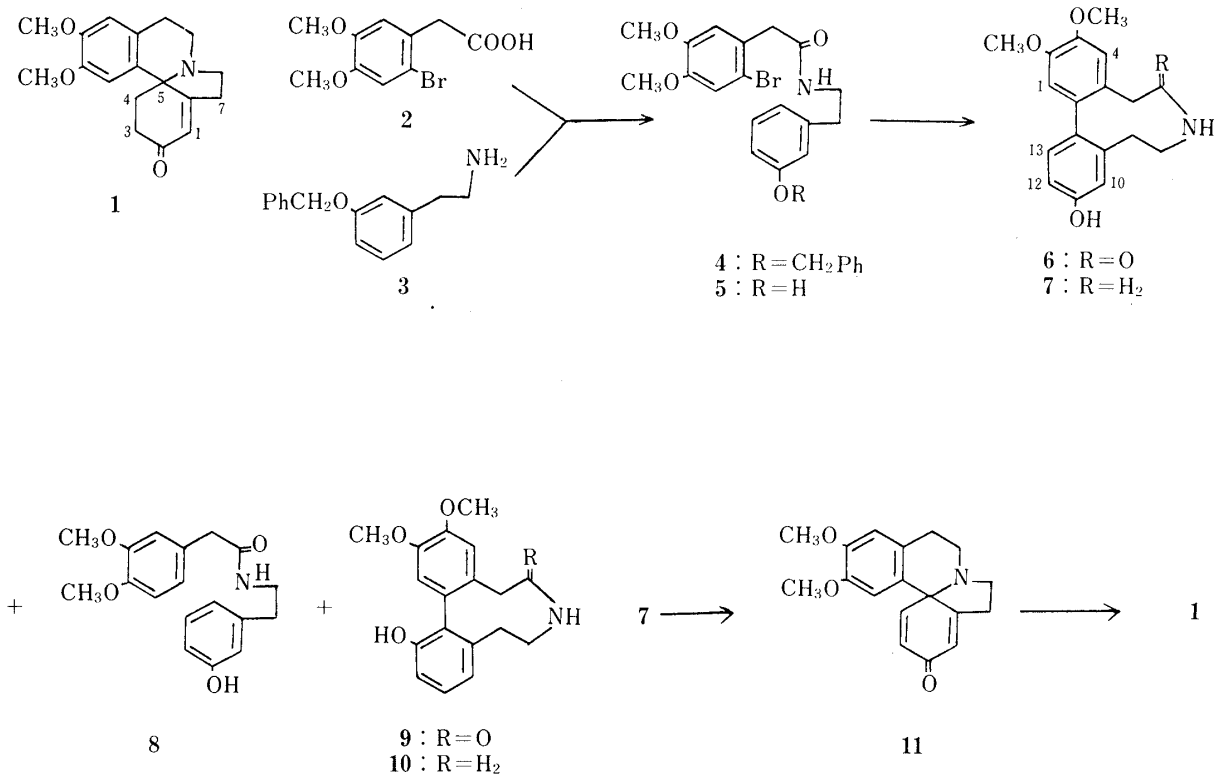

Chart 1

of **7** in the aromatic region exhibited a typical ABX-type signal (δ 6.60, d, $J=2$ Hz; 6.76, dd, $J=2$, 8 Hz; 6.99, d, $J=8$ Hz) together with two singlets (δ 6.61 and 6.65). Therefore, the major product and the secondary amine are shown to have the structures **6** and **7**, respectively, so that the photochemical coupling reaction occurred at the *para* position with respect to the hydroxyl group in **5**.

The minor product (**8**), mp 132—133 °C, $C_{18}H_{21}NO_4$, showed the molecular peak at *m/z* 315 in the MS and its IR spectrum revealed the absorption of a hydroxyl group (3580 cm^{-1}) and an amide group (3410 and 1650 cm^{-1}). The NMR spectrum exhibited the signals of two methoxyl groups (δ 3.76 and 3.81), three methylene groups (δ 3.44, 3.47 and 3.67) and seven aromatic protons (δ 6.44—7.18). This product was assigned the structure **8** which corresponds to **5** minus the bromine atom. This debromination product (**8**) was confirmed to be *N*-(3-hydroxyphenethyl)-2-(3,4-dimethoxyphenyl)acetamide by direct comparison with an authentic specimen, prepared by hydrogenation of **5** with 10% Pd–C.

The third product (**9**), mp 252—254 °C, $C_{18}H_{19}NO_4$, also had an amide group and a hydroxyl group, like compounds **6** and **8**. The NMR spectrum showed a pattern very similar to that of **6** except for the aromatic region. The substitution pattern of the aromatic ring was clarified by NMR measurement of the reduction product (**10**), synthesized by reduction of **9** with diborane. Signals of three aromatic protons in the NMR spectrum of **10** were assigned to H_{10} and H_{12} (δ 6.78, 2H, d, $J=7$ Hz) and H_{11} (δ 6.82, 1H, t, $J=7$ Hz) and the other two aromatic protons gave singlet signals at δ 6.67 and 6.69. Thus, in these compounds (**9** and **10**) it is clear that the photochemical reaction occurred at the *ortho* position to the hydroxyl group in **5** supporting the proposed structure of **9**.

Next, in order to complete the synthesis of 3-demethoxyerythratidinone (**1**) we investigated the oxidation of the phenolic amine (**7**) to yield a desired dienone compound (**11**). The results of a series of oxidation experiments are summarized in Table I.

When the phenolic amine (**7**) was treated under various oxidation conditions employing

Table I. Oxidation of **7** to **11**

Oxidant	Product (Yield %)	Oxidant	Product (Yield %)
PbO_2	65	AgO	7
$K_3Fe(CN)_6$	60	$Pb(OAc)_4$	Trace
MnO_2	47	MTA	Trace
TTFA	27	$VOCl_3$	—[a]
Ag_2CO_3/celite	8	Ag_2O	—[a]

a) No oxidation occurred.

vanadium oxytrichloride,[8] and silver oxide,[9] the starting material was recovered unchanged. On oxidation with lead tetraacetate,[10] MTA (manganic trisacetylacetonate),[11] silver(II)-oxide,[12] and Fetizon reagent (silver carbonate–celite),[13] the amine (**7**) provided a small amount of the desired dienone (**11**) together with other products showing many spots on thin-layer chromatography (TLC) analysis. It was finally found that oxidation of **7** with active lead dioxide,[14] active manganese dioxide,[15] and potassium ferricyanide[4,16] gave the dienone (**11**) as a main reaction product. In particular, oxidation of **7** with a two-phase system of chloroform and aqueous potassium ferricyanide in the presence of sodium hydrogen carbonate gave the dienone (**11**) in 60% yield, and reaction with active lead dioxide in benzene under reflux also afforded **11** in 65% yield. The IR spectrum of **11** revealed the characteristic dienone group at 1670 and 1645 cm^{-1} and the NMR spectrum also exhibited the characteristic signals of a dienone system (δ 6.04, dd, J=2, 9 Hz; 6.17, d, J=2 Hz; 7.01, d, J=9 Hz).

Finally, catalytic hydrogenation of **11** in ethanol with Pd–C gave a dihydro derivative (**1**), mp 110 °C, in 88% yield. The IR, NMR and MS of **1** were identical with those of the natural product, 3-demethoxyerythratidinone.[5] Thus, we have achieved a convenient synthesis of 3-demethoxyerythratidinone (**1**) *via* formation of the dibenzazonine skeleton followed by a phenol oxidation reaction.

Experimental

All melting points were determined on a Yanagimoto micromelting point apparatus, and are uncorrected. IR spectra were measured on a JASCO IRA-3 spectrometer and NMR spectra were recorded on a JEOL PS-100 spectrometer with tetramethylsilane as an internal standard. Abbreviations used: s=singlet, d=doublet, t=triplet, m=multiplet, and dd=double doublet. Mass spectra (MS) were taken with a Hitachi M-52 spectrometer with a direct inlet system. Column chromatography was performed with Merck silica gel 60 (70—230 mesh). TLC was carried out by using a 0.25 mm thickness of Merck silica gel 60F-254.

***N*-(3-Benzyloxyphenethyl)-2-(6-bromo-3,4-dimethoxyphenyl)acetamide (4)**——A mixture of **3** (2.3 g), **2**[6] (2.0 g), and decalin (80 ml) was heated under reflux for 2 h. The mixture was evaporated to dryness and the residue was dissolved in $CHCl_3$. The $CHCl_3$ solution was washed in turn with dil. hydrochloric acid, dil. NaOH and water, then dried over Na_2SO_4, and evaporated. The crude solid was crystallized from ether. Colorless needles. mp 121 °C (3.4 g) (97%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3410 (NHCO), 1660 (NHCO). *Anal.* Calcd for $C_{25}H_{26}BrNO_4$: C, 61.99; H, 5.41; N, 2.89. Found: C, 62.11; H, 5.38; N, 2.70.

2-(6-Bromo-3,4-dimethoxyphenyl)-*N*-(3-hydroxyphenethyl)acetamide (5)——A mixture of **4** (3.2 g), conc. hydrochloric acid (30 ml), and EtOH (30 ml) was heated for 2 h at 70 °C. The mixture was evaporated and the resulting brown oil was dissolved in $CHCl_3$. The $CHCl_3$ solution was dried over Na_2SO_4 and evaporated. The residue was recrystallized from acetone. Colorless needles. mp 169 °C (2.3 g) (88%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 3420 (NHCO), 1660 (NHCO). *Anal.* Calcd for $C_{18}H_{20}BrNO_4$: C, 54.84; H, 5.11; N, 3.55. Found: C, 54.89; H, 5.11; N, 3.34.

Irradiation of 2-(6-Bromo-3,4-dimethoxyphenyl)-*N*-(3-hydroxyphenethyl)acetamide (5)——A mixture of **5** (800 mg), NaOH (650 mg), and MeOH (250 ml) was irradiated with a 100 W high pressure mercury lamp (Taika Industry Co., HLV-B type) under a nitrogen atmosphere for 2 h at room temperature. The mixture was evaporated and neutralized with hydrochloric acid, followed by extraction with $CHCl_3$. The $CHCl_3$ layer was dried over Na_2SO_4 and evaporated to give a brownish oil. The oil was crystallized from a mixture of ethyl acetate and acetone to afford a

solid (**6**). The solid was recrystallized from MeOH.Colorless needles. mp 297—298 °C (360 mg) (57%). TLC (silica gel/$CHCl_3$–acetone 1 : 1 (v/v), $Rf=0.36$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 3400 (NHCO), 1650 (NHCO). NMR (DMSO-d_6) δ: 3.73, 3.78 (6H, 2×s, 2×OCH_3), 6.42—7.38 (5H, m, arom. H). MS *m/z*: 313 [M^+] (100%), 283, 256, 241, 213, 195. *Anal.* Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11; N, 4.47. Found. C, 68.89; H, 6.10; N, 4.27.

The mother liquor, from which the crude solid (**6**) had been removed by filtration, was chromatographed on a silica gel column and eluted with a mixture of $CHCl_3$ and acetone (5 : 1). A solid obtained from the first fraction was recrystallized from benzene to give **8**. Colorless needles. mp 132—133 °C (25 mg) (4%). TLC (silica gel/$CHCl_3$–acetone 1 : 1 (v/v), $Rf=0.64$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580 (OH), 3410 (NHCO), 1650 (NHCO).NMR ($CDCl_3$) δ: 3.44 (2H, q, $J=7$ Hz, $ArCH_2\underline{CH_2}N$), 3.47 (2H, s, $Ar\underline{CH_2}CO$), 3.67 (2H, t, $J=7$ Hz, $Ar\underline{CH_2}CH_2N$), 3.76, 3.81 (6H, 2×s, 2×OCH_3), 5.94 (1H, t, $J=7$ Hz, NH), 6.44—7.18 (7H, m, 7×arom. H). MS *m/z*: 315 [M^+], 256, 236, 195, 151 (100%). *Anal.* Calcd for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.62; H, 6.76; N, 4.33.

The next fraction was evaporated to afford a solid (**9**), which was recrystallized from MeOH. Colorless prisms. mp 252—254 °C (80 mg) (13%). TLC (silica gel/$CHCl_3$–acetone 1 : 1 (v/v), $Rf=0.44$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3545 (OH), 3410 (NHCO), 1655 (NHCO). NMR ($CDCl_3$) δ: 3.85, 3.96 (6H, 2×s, 2×OCH_3), 6.56—7.48 (5H, m, 5×arom. H). MS *m/z*: 313 [M^+] (100%), 284, 256, 241, 213, 195. *Anal.* Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11; N, 4.47. Found: C, 69.21; H, 6.09; N, 4.36.

5,6,8,9-Tetrahydro-2,3-dimethoxy-7*H*-dibenz[*d*,*f*]azonin-11-ol (7)——BF_3–etherate (0.5 ml) was added dropwise to a cold mixture of **6** (200 mg), $NaBH_4$ (100 mg) and THF (80 ml) under a nitrogen atmosphere with stirring. The whole mixture was allowed to stand at room temperature overnight. After being cooled, the reaction mixture was decomposed with EtOH, water, and conc. hydrochloric acid, and evaporated to dryness. The residual oil was neutralized with NH_4OH and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water, dried over Na_2SO_4, and evaporated to afford **7**. The solid was recrystallized from acetone. Colorless needles. mp 205—207 °C (177 mg) (93%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3565 (OH). NMR ($CDCl_3$) δ: 3.81, 3.89 (6H, 2×s, 2×OCH_3), 6.60 (1H, d, $J=2$ Hz, C_{10}–H), 6.61, 6.65 (2H, 2×s, C_1–H, C_4–H), 6.76 (1H, dd, $J=2$, 8 Hz, C_{12}–H), 6.99 (1H, d, $J=8$ Hz, C_{13}–H). MS *m/z*: 299 [M^+] (100%), 284, 279, 257, 242, 226. *Anal.* Calcd $C_{18}H_{21}NO_3$: C, 72.21; H, 7.07; N, 4.68. Found: C, 72.01; H, 6.98; N, 4.55.

5,6,8,9-Tetrahydro-2,3-dimethoxy-7*H*-dibenz[*d*,*f*]azonin-13-ol (10)——A solution of **9** (25 mg) in THF (20 ml) was reduced with $NaBH_4$ (20 mg) and BF_3–etherate (0.1 ml) in the same way as **6** to provide **10**. Colorless oil. (21 mg) (88%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3565 (OH). NMR ($CDCl_3$) δ: 3.84, 3.92 (6H, 2×s, 2×OCH_3), 6.69, 6.67 (2H, 2×s, C_1–H, C_4–H), 6.78 (2H, d, $J=7$ Hz, C_{10}–H, C_{12}–H), 6.82 (1H, t, $J=7$ Hz, C_{11}–H). MS *m/z*: 299 [M^+] (100%), 284, 257, 242, 226.

Hydrogenation of 5——A solution of **5** (50 mg) and conc. hydrobromic acid (3 drops) in MeOH (20 ml) was hydrogenated over 10% Pd–C (30 mg) under an H_2 atmosphere at room temperature for 1 h. The catalyst was filtered off and the solvent was removed to afford a solid. The solid was recrystallized from benzene. Colorless needles. mp 131—132 °C (35 mg) (88%). This compound was found to be identical with the photolysis product (**8**) by mixed melting point determination and comparison of their IR and NMR spectra.

15,16-Dimethoxyerythrinan-1,3-dien-2-one (11)——a) Oxidation of **7** with $K_3Fe(CN)_6$:[16] A solution of **7** (40 mg) in $CHCl_3$ (20 ml) was added dropwise to a stirred solution of $K_3Fe(CN)_6$ (350 mg) in 5% $NaHCO_3$ (25 ml) during 20 min at room temperature, and the resulting mixture was heated at 45 °C for 30 min. After cooling, the mixture was filtered through celite. The organic layer was separated, the aqueous layer was extracted with $CHCl_3$, and the combined organic layers were washed with H_2O, dried over Na_2SO_4, and evaporated to leave a brownish oil, which was chromatographed on silica gel. Elution with a mixture of $CHCl_3$ and acetone (10 : 1) afforded a colorless oil (**11**) (24 mg) (60%). TLC (silica gel/$CHCl_3$–acetone 10 : 1 (v/v), $Rf=0.13$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1670, 1645 (dienone). NMR ($CDCl_3$) δ: 3.64, 3.77 (6H, 2×s, 2×OCH_3), 6.04 (1H, dd, $J=2$, 9 Hz, C_3–H), 6.17 (1H, d, $J=2$ Hz, C_1–H), 6.32, 6.48 (2H, 2×s, 2×arom. H), 7.01 (1H, d, $J=9$ Hz, C_4–H). MS *m/z*: 297 [M^+] (100%), 282, 254.

b) Oxidation of **7** with PbO_2:[14] Freshly prepared PbO_2[17] (400 mg) was added to a solution of **7** (40 mg) in benzene (15 ml) in one portion and the mixture was stirred at room temperature for 1 h, then filtered through celite. The filtrate was evaporated to give an oil, which was purified by chromatography in a manner similar to that described in a) to afford **11** (26 mg) (65%) as a colorless oil. Spectral (IR, NMR, and MS) properties of this oxidation product were identical with those of the product obtained in a).

c) Oxidation of **7** with MnO_2:[15] Freshly prepared MnO_2[15] (300 mg) was added gradually to a solution of **7** (30 mg) in ether (5 ml) and acetone (5 ml), and the mixture was stirred at room temperature overnight, then treated in the same way as in a) to yield **11** (14 mg) (47%). IR, MS, and NMR spectra of this oxidation product were superimposable on those of the product obtained in a).

d) Oxidation of **7** with TTFA:[18] **7** (30 mg) was added to a solution of TTFA (thallium trifluoroacetate) (45 mg) and CH_2Cl_2 (8 ml) and the mixture was stirred at room temperature for 3 h. The organic solvent was evaporated off *in vacuo* to give a brownish oily residue, which was purified by chromatography to yield a colorless oil (**11**) (8 mg) (27%). Spectral (IR, NMR, and MS) properties of this product were superimposable on those of an authentic sample of **11**.

e) Oxidation of **7** with Fetizon Reagent:[13] Fetizon reagent (Ag_2CO_3 on celite)[13] (50 mg) was added to a solution of **7** (15 mg) in benzene (15 ml) and the mixture was heated under reflux for 2 h. An insoluble material,

consisting mainly of silver on celite, was filtered off and washed with benzene. The combined filtrate and washings were concentrated to yield a reddish-brown solid, which was purified by chromatography to afford a colorless oil (**11**) (1.2 mg) (8%). This substance was identical with the authentic sample prepared in a) on the basis of spectral (IR, NMR, and MS) comparisons.

f) Oxidation of **7** with AgO:[12] AgO[12] (15 mg) was added to a solution of **7** (15 mg) in benzene (5 ml) and the mixture was stirred at room temperature overnight. An insoluble material was filtered off and washed with benzene. The combined filtrate and washings were washed with water, dried over Na_2SO_4, and evaporated to give a brownish oil, which was purified by chromatography to yield a colorless oil (**11**) (1.0 mg) (7%). Spectral (IR, NMR, and MS) properties of this compound were superimposable on those of the product obtained in a).

3-Demethoxyerythratidinone (1)——A solution of **11** (27 mg) in EtOH (15 ml) was hydrogenated over 5% Pd–C (10 mg) under H_2 at room temperature overnight. The mixture was filtered and the filtrate was evaporated to afford a solid (**1**). This solid was recrystallized from petroleum ether. Colorless needles. mp 110 °C (24 mg) (88%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1665 cm^{-1} (CO). NMR ($CDCl_3$) δ: 3.70, 3.80 (6H, 2 × s, 2 × OCH_3), 6.06 (1H, m, C_1–H), 6.56, 6.62 (2H, 2 × s, 2 × arom. H). MS *m/z*: 299 [M^+], 271 (100%), 242, 212, 197. Spectra (IR, NMR, and MS) of this reduction product were superimposable on those of an authentic specimen.[5]

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