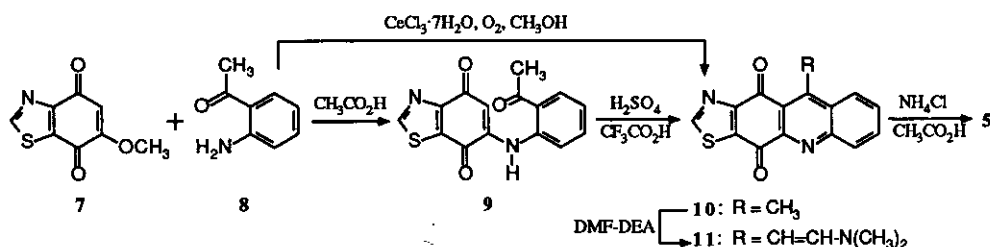
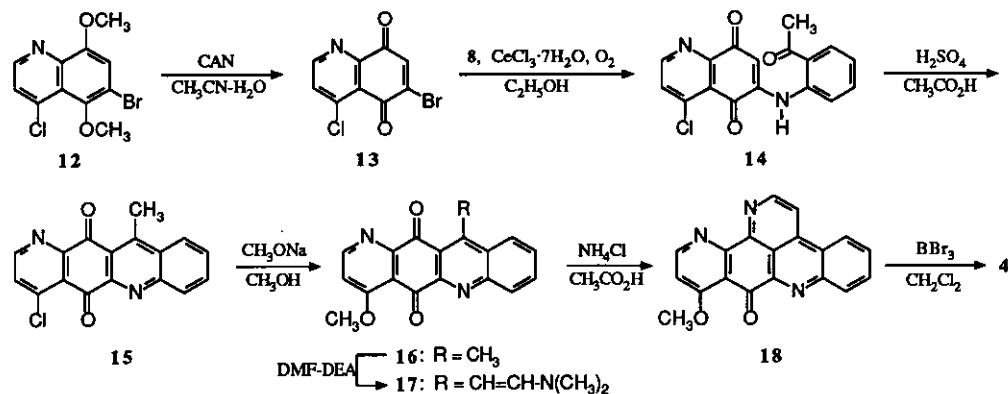


cyclization product (**10**) was directly obtained in 73% yield. The tetracyclic quinone (**10**) was heated with *N,N*-dimethylformamide diethyl acetal (DMF-DEA) in *N,N*-dimethylformamide (DMF)^{7a} at 110°C for 30 min to give **11**. Treatment of **11** with ammonium chloride in acetic acid at 110°C for 30 min furnished the pentacyclic iminoquinolinequinone (**5**)⁹ in 47% yield from **10**. The spectral data of synthetic iminoquinolinequinone (**5**) were identical with those of kuanoniamine A obtained from natural resources.

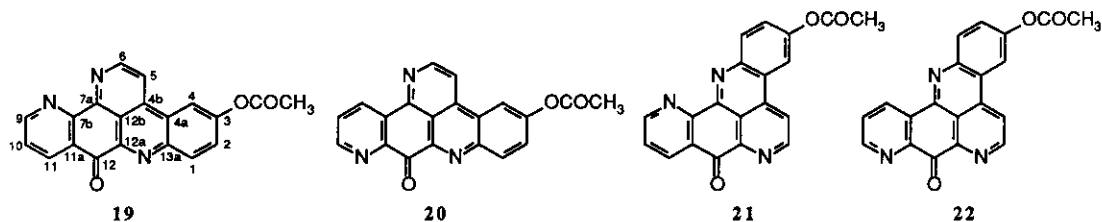


Next, we synthesized 11-hydroxyascididemin (**4**) isolated from *Leptoclinides* sp. from Truk Lagoon.^{2d} Oxidative demethylation of 6-bromo-4-chloro-5,8-dimethoxyquinoline (**12**)¹⁰ with cerium (IV) ammonium nitrate (CAN) in aqueous acetonitrile (20°C, 10 min) gave 5,8-quinolinedione (**13**) in 56% yield. The quinone (**13**) was condensed with 2-aminoacetophenone (**8**) in ethanol containing cerium (III) chloride under air (20°C, 4 h) to give **14** in 74% yield. The cyclization of **14** with 10% sulfuric acid in acetic acid (62–63°C, 1 h) gave the tetracyclic quinone (**15**) in 69% yield. On treating with sodium methoxide in methanol (20°C, 30 min), the chlorine atom in **15** was substituted by a methoxyl group in a quantitative yield. Treatment of **16** with DMF-DEA in DMF (120°C, 15 min) followed by ammonium chloride in acetic acid (120°C, 10 min) furnished the pentacyclic iminoquinolinequinone (**18**) in 31% yield. The methyl ether in **18** was cleaved with boron tribromide in dichloromethane (–10 — –20°C, 1 h) to furnish **4**.¹¹ The spectral data of synthetic **4** were identical with those of 11-hydroxyascididemin obtained from a natural resource.

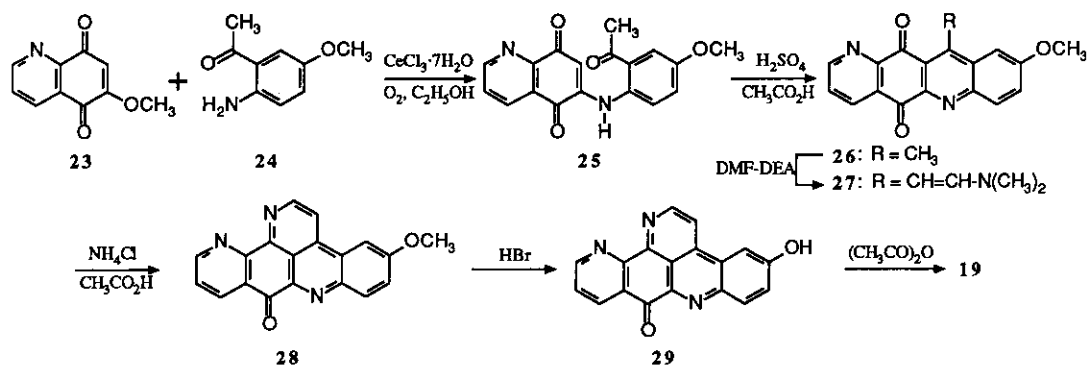


Finally, we determined the structure of neocallactine acetate by unambiguous total synthesis. Neocallactine acetate is a derivative prepared from callactine, a pigment isolated from the sea anemone *Calliactis parasitica*,

and four alternative structures (19-22) were proposed.³ Last year, Schmitz *et al.* reported further structural elucidation of neocalliactine acetate by a comparison with ¹H- and ¹³C- nmr spectral data of meridine (2), ascididemin (3), and 11-hydroxyascididemin (4).^{2d} They ruled out 21 and 22 possessing the meridine ring array unequivocally, and slightly preferred 19 of the two remaining structures having the overall skeletal outline of ascididemin (3). Thus, we studied the synthesis of 19.



Treatment of 6-methoxy-5,8-quinolinedione (23)¹² with 2-amino-5-methoxyacetophenone (24)¹³ in ethanol containing cerium (III) chloride under air (20°C, 1 h) gave 25 in 46% yield. The anilinoquinone (25) was heated with concentrated sulfuric acid in acetic acid (90°C, 30 min) to give the cyclization product (26) in 94% yield. Reaction of 26 with DMF-DEA in DMF (120°C, 30 min) followed by treatment with ammonium chloride in acetic acid (120°C, 30 min) furnished 28 in 64% yield. The methyl ether (28) was refluxed in 48% hydrobromic acid for 4 h to give 29. The acetylation of phenol (29) with acetic anhydride in pyridine (20°C, 2 h) furnished the acetate (19) in 39% yield from 28. The spectral data of synthetic acetate (19)¹⁴ were identical with those of neocalliactine acetate. Thus, we determined the structure of neocalliactine acetate to be 19, *i.e.* 3-acetoxyascididemin.



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9. **5**: mp 258-259°C (CHCl₃) (lit.,^{2f} mp 255-258°C (decomp.)). Ms *m/z* (%): 289 (M⁺, 100). High-resolution ms Calcd for C₁₆H₇N₃OS: 289.0310. Found: 289.0315. ¹H-Nmr (270 MHz, DMSO-*d*₆) δ: 8.03 (1H, t, *J* = 8.3 Hz, C₅-H), 8.09 (1H, t, *J* = 8.3 Hz, C₆-H), 8.43 (1H, d, *J* = 8.3 Hz, C₇-H), 8.84 (1H, d, *J* = 5.9 Hz, C₃-H), 8.96 (1H, d, *J* = 8.3 Hz, C₄-H), 9.11 (1H, d, *J* = 5.9 Hz, C₂-H), 9.68 (1H, s, C₁₁-H).
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11. **4**: mp >260°C (CHCl₃) (lit.,^{2d} mp >250°C). Ms *m/z* (%): 299 (M⁺, 93), 271 (100). High-resolution ms Calcd for C₁₈H₉N₃O₂: 299.0695. Found: 299.0715. ¹H-Nmr (270 MHz, CDCl₃) δ: 7.15 (1H, d, *J* = 5.6 Hz, C₉-H), 8.00 (1H, dt, *J* = 8.3, 1.3 Hz, C₃-H), 8.07 (1H, dt, *J* = 8.3, 1.7 Hz, C₂-H), 8.59 (1H, d, *J* = 5.6 Hz, C₅-H), 8.65 (1H, dd, *J* = 8.3, 1.3 Hz, C₁-H), 8.73 (1H, dd, *J* = 8.3, 1.7 Hz, C₄-H), 8.90 (1H, d, *J* = 5.6 Hz, C₁₀-H), 9.32 (1H, d, *J* = 5.6 Hz, C₆-H), 13.06 (1H, s, OH).
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14. **19**: mp >270°C (decomp.) (CHCl₃-ether) (lit.,³ no mp was given). Ms *m/z* (%): 341 (M⁺, 13), 313 (22), 299 (100). High-resolution ms Calcd for C₂₀H₁₁N₃O₃: 341.0800. Found: 341.0800. ¹H-Nmr (270 MHz, CDCl₃-CD₃OD) δ: 2.39 (3H, s, CH₃), 7.66 (1H, dd, *J* = 7.9, 4.6 Hz, C₁₀-H), 7.72 (1H, dd, *J* = 8.9, 2.3 Hz, C₂-H), 8.42 (1H, d, *J* = 2.3 Hz, C₄-H), 8.47 (1H, d, *J* = 5.9 Hz, C₅-H), 8.54 (1H, d, *J* = 8.9 Hz, C₁-H), 8.72 (1H, dd, *J* = 7.9, 1.6 Hz, C₁₁-H), 9.08 (1H, dd, *J* = 4.6, 1.6 Hz, C₉-H), 9.18 (1H, d, *J* = 5.9 Hz, C₆-H). ¹³C-Nmr (67.8 MHz, CDCl₃-CD₃OD) δ: 20.80 (CH₃), 115.03 (C₄), 117.18 (C₅), 117.72 (C_{12b}), 124.42 (C_{4a}), 125.82 (C₁₀), 126.71 (C₂), 128.81 (C_{11a}), 133.99 (C₁), 136.54 (C₁₁), 137.68 (C_{4b}), 143.20 (C_{13a}), 145.25 (C_{12a}), 149.24 (C_{7a}), 149.31 (C₆), 151.67 (C_{7b}), 152.24 (C₃), 155.15 (C₉), 169.05 (CH₃CO), 181.33 (C₁₂).