dropwise. Cleavage of the enol silane was monitored by GC or TLC. After 1 h the solution was cooled to −78 °C (dry ice–acetone bath), and a solution of 0.35 g (1.2 mmol, 1.2 equiv based on enol silane) of (+)-**13b** in 10 mL of THF was added dropwise. After 30 min at −78 °C the mixture was quenched by addition of 3 mL of a saturated aqueous $NH_4Cl$ solution followed by 3 mL of saturated $NH_4I$ solution. The solution was brought to room temperature and diluted with 20 mL of ethyl acetate. The organic layer was washed successively with saturated $Na_2S_2O_3$ solution and brine, 2 × 15 mL, and dried. Concentration in vacuo gave an oil that was stirred with three portions of *n*-pentane (3 mL) and filtered to remove the (camphorsulfonyl)imine **8b** byproduct. Purification of the residue by preparative TLC or flash chromatography (pentane/$Et_2O$, 60:40) gave 0.06 g (45%) of (*S*)-(+)-2-hydroxy-1-phenyl-1-propanone (**17a**): >95% ee; $[\alpha]^{20}_D$ = −79.8° (*c* = 1.3, $CHCl_3$) [lit.[22] $[\alpha]^{20}_D$ = −80.9° (*c* = 2.0, $CHCl_3$)].

Oxidation of the *E*-silyl enol ether **22** (93:7 *E*:*Z*)[30] was carried out in a similar manner except that there was no reaction at −78 °C and warming to −45 °C was required. Standard workup gave 0.76 g (51%) of (*S*)-**17a**, 23% ee $[\alpha]^{20}_D$ −20.65° (*c* = 1.8, $CHCl_3$).

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# Total Synthesis of Montanine-Type *Amaryllidaceae* Alkaloids, Which Possess a 5,11-Methanomorphanthridine Ring System, through Cyclization with Sodium Bis(2-methoxyethoxy)aluminum Hydride: The First Stereoselective Total Syntheses of (±)-Montanine, (±)-Coccinine, (±)-*O*-Acetylmontanine, (±)-Pancracine, and (±)-Brunsvigine[1]

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The stereoselective total syntheses of the title alkaloids **1**–**5** from allylic chloride **31** are described. The key steps in the reaction sequences are as follows: (1) stereoselective hydroboration–oxidation of **12** by means of an intramolecular charge-transfer complex to afford alcohol **13** as a single isomer; (2) cyclization of tosylamide alcohol **21** with sodium bis(2-methoxyethoxy)aluminum hydride (SMEAH) to afford functionalized 5,11-methanomorphanthridine **22**, which possesses the basic skeleton of montanine-type alkaloids; and (3) conversion of **30a** to allylic chloride **31** by treatment with PhSeCl in MeOH under ultrasonication followed by $NaIO_4$ oxidation. A formal total synthesis of (±)-manthine (**6**) was also accomplished.

## Introduction

Montanine-type alkaloids such as montanine (**1**),[2] coccinine (**2**),[2] *O*-acetylmontanine (**3**),[3] pancracine (**4**),[4] and brunsvigine (**5**)[5a] have a 5,11-methanomorphanthridine ring system unique among the *Amaryllidaceae* alkaloids.[6] Montanine-type alkaloids are attractive synthetic targets for synthetic chemists because of their unique architectures and their pharmacological promise.[7] Although there is a report[8] on synthetic studies of montanine-type alkaloids, synthesis of the 5,11-methanomorphanthridine ring system other than by conversion[2b] of haemanthamine to manthine (**6**) has been unsuccessful. However, very recently, we succeeded in a synthesis of the ring system[9] and the total syntheses[1] of (±)-montanine (**1**), (±)-coccinine (**2**), and (±)-pancracine (**4**). Concurrently, a total synthesis of (±)-pancracine (**4**) was reported by Overman and Shim.[10]

In the present paper, we describe stereoselective total syntheses of the title alkaloids, (±)-montanine (**1**), (±)-coccinine (**2**), (±)-*O*-acetylmontanine (**3**), (±)-pancracine (**4**), and (±)-brunsvigine (**5**), using as the key step reductive cyclization of tosylamide alcohol **21** with sodium bis(2-methoxyethoxy)aluminum hydride (SMEAH) to afford functionalized 5,11-methanomorphanthridine **22**. A retrosynthetic analysis for these alkaloids is depicted in Scheme I.

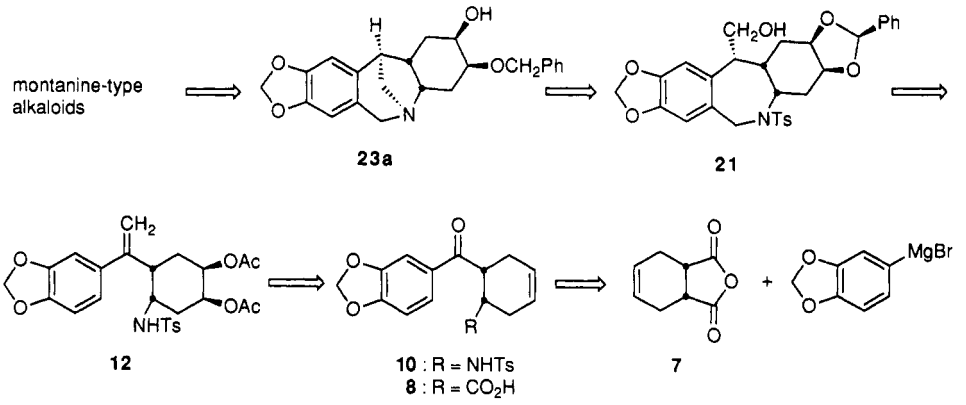
## Results and Discussion

**Synthesis of Key Compound 23a.** Synthesis of key compound **23a** was carried out as follows (Scheme II). Reaction of *cis*-cyclohexenedicarboxylic acid anhydride **7** with 3,4-(methylenedioxy)phenylmagnesium bromide in tetrahydrofuran (THF) at 0 °C afforded keto acid **8** in 96% yield. Keto acid **8** was converted to the acid azide, and

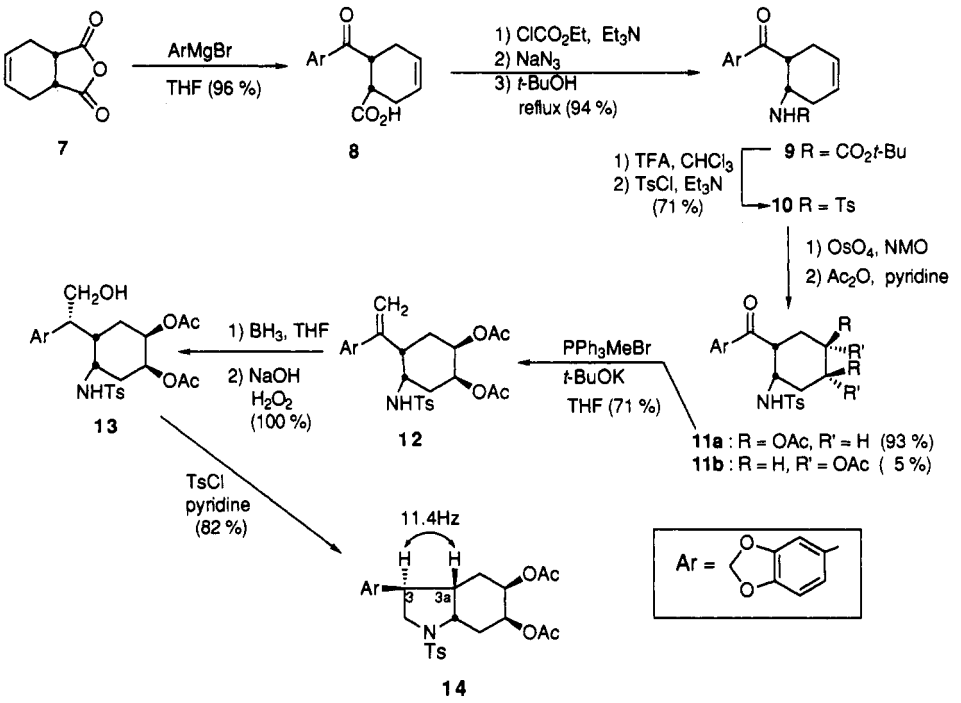
(1) For preliminary communication of a part of this work, see: Ishizaki, M.; Hoshino, O.; Iitaka, Y. *Tetrahedron Lett.* **1991**, *32*, 7079.
(2) (a) Wildman, W. C.; Kaufman, C. J. *J. Am. Chem. Soc.* **1955**, *77*, 1248. (b) Inubushi, Y.; Fales, H. M.; Warnhoff, E. W.; Wildman, W. C. *J. Org. Chem.* **1960**, *25*, 2153.
(3) Wildman, W. C.; Brown, C.; Michei, K.-H.; Bailey, D.; Heimer, N.; Walffer, R. Murphy, C. *Pharmazie* **1967**, *22*, 725.
(4) Sandberg, F.; Michel, K.-H. *Lloydia* **1963**, *26*, 78.
(5) (a) Dry, L. J.; Poynton, M.; Thompson, M. E.; Warren, F. L. *J. Chem. Soc.* **1958**, 4701. (b) Laing, M.; Clark, R. C. *Tetrahedron Lett.* **1974**, 583. (c) Clark, R. C.; Warren, F. L. *Tetrahedron* **1975**, *31*, 1855.
(6) Martin, S. F. In *The Alkaloids*; Brossi, A. R., Ed.; Academic Press: New York, 1987; Vol. 30, Chapter 2.
(7) Cf. Dictionary of Alkaloids; Southon, I. W., Buckingham, J., Eds.; Chapman and Hall: London, 1989; C-00291, M-00331.
(8) Sanchez, I. H.; Larraza, M. I.; Rojas, I.; Brena, F. K.; Flores, H. J. *Heterocycles* **1985**, *23*, 3033.
(9) (a) Hoshino, O.; Ishizaki, M. *Chem. Lett.* **1990**, 1817. (b) Hoshino, O.; Ishizaki, M.; Saito, K.; Yumoto, K. *J. Chem. Soc., Chem. Commun.* **1990**, 420.
(10) Overman, L. E.; Shim, J. *J. Org. Chem.* **1991**, *56*, 5005.

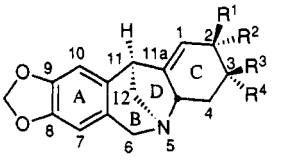
0022-3263/92/1957-7285$03.00/0 

**Scheme I. Retrosynthesis**




**Scheme II**



| | R1 | R2 | R3 | R4 |
|---|---|---|---|---|
| montanine 1 | H | OMe | OH | H |
| coccinine 2 | OMe | H | OH | H |
| O-acetylmontanine 3 | H | OMe | OAc | H |
| pancracine 4 | H | OH | OH | H |
| brunsvigine 5 | H | OH | H | OH |
| manthine 6 | H | OMe | OMe | H |

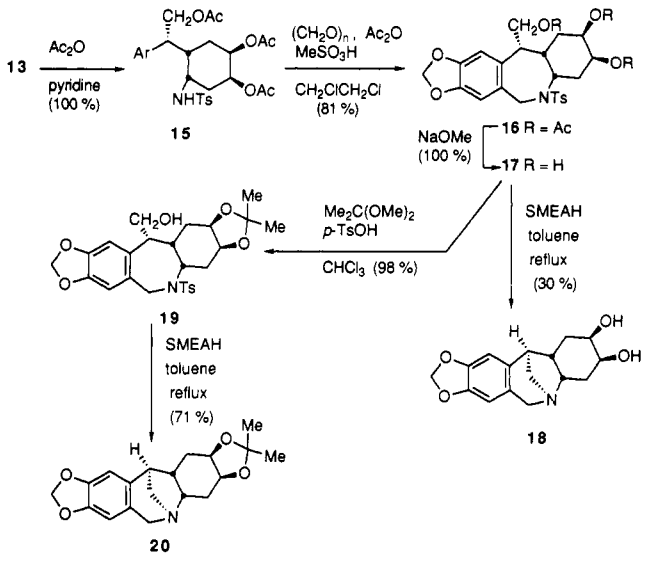
**Figure 1.** X-ray structure of benzylidene acetal **22**.

subsequent Curtius rearrangement in boiling 2-methyl-2-propanol for 24 h gave carbamate **9** in 94% yield. Treatment of **9** with trifluoroacetic acid and subsequent tosylation gave tosylamide **10** in 71% yield. As the C-3 hydroxyl group is β-oriented in all the alkaloids (1–4) except for brunsvigine (5), introduction of a β-hydroxyl group was a necessary requirement. From inspection of the Dreiding model of **10**, we anticipated that cis-dihydroxylation would occur from the β-face of the cyclohexene ring in **10**. As we anticipated, osmium oxidation[11] in dioxane–$H_2O$ (4:1) occurred stereoselectively to give, after acetylation, β-diacetate **11a** (93%) accompanied by a small amount of α-diacetate **11b** (5%). Oxidation in acetone–$H_2O$ (4:1) and in THF–$H_2O$ (4:1) followed by acetylation gave **11a** and **11b** in ratios of 2:1 and 2.5:1, respectively. The stereochemistry of major product **11a** was determined by its conversion to **22** as discussed below.

Next, to produce a precursor for reductive cyclization, Wittig olefination and hydroboration–oxidation were performed. Wittig reaction of **11a** in the usual manner afforded **12** in 71% yield; hydroboration–oxidation of **12** at 0 °C for 1 h gave a single isomer (**13**) in quantitative yield. The stereochemistry of **13** was determined from the $^1H$ NMR spectrum of octahydroindoline **14**, derived from **13** by treatment of **13** with *p*-toluenesulfonyl chloride in pyridine; the vicinal coupling constant between the C-3 and C-3a hydrogens in **14** is 11.4 Hz (trans-orientation). In this case, as well as in those reported previously,[1,9a] hydroboration occurred stereoselectively from the β-face of the *exo*-methylene group in **12**. The stereoselectivity of the reaction was attributable to formation of a

(11) VonRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, *23*, 1973.

**Scheme III**




charge-transfer complex between the electron-rich 3,4-(methylenedioxy)phenyl group and the electron-deficient *p*-tosyl group. This hypothesis was supported by the $^1$H NMR spectrum of **12** in which the aromatic protons due to the 3,4-(methylenedioxy)phenyl group resonated at $\delta$ 6.40–6.56.[12]

To transform of **13** to 5,11-methanomorphanthridine **18** according to the procedure[9] reported previously, **13** was converted to tosylamide triacetate **16** (81%) by a modified Pictet–Spengler reaction[13] of triacetate **15** (Scheme III). The reaction of tosylamide triacetate **16** with SMEAH in refluxing toluene gave a complex mixture, and triol **17** produced **18** in only 30% yield. The results suggested that the aluminum complex generated by the reaction of SMEAH with the vicinal hydroxyl groups in **16** or **17** interfered with the cyclization reaction. Therefore, the vicinal hydroxyl groups in **17** were protected with an isopropylidene group in the usual manner to afford acetonide **19** in 98% yield. The cyclization reaction of **19** afforded the corresponding functionalized 5,11-methanomorphanthridine **20** in 71% yield.

Introduction of a hydroxyl group at C-3 and a double bond between C-1 and C-11a was required in the next step. Since regioselective cleavage of the protecting group in 5,11-methanomorphanthridine **20** was desired, the vicinal hydroxyl groups in **17** were protected with a benzylidene instead of an isopropylidene group. Thus, treatment of **17** with benzaldehyde dimethyl acetal in the presence of acid produced benzylidene acetal **21** as a single diastereomer in 83% yield (Scheme IV). Reaction of **21** with SMEAH in refluxing *o*-xylene for 35 min afforded the corresponding 5,11-methanomorphanthridine **22** in 91% yield, whereas the reaction in refluxing toluene required 2 h to furnish **22** (71%). 5,11-Methanomorphanthridine **22** was also obtained from **18** in the manner described for the conversion of **17** to **21**. The structure and stereochemistry of **22** were confirmed by X-ray crystallographic analysis (Figure 2).

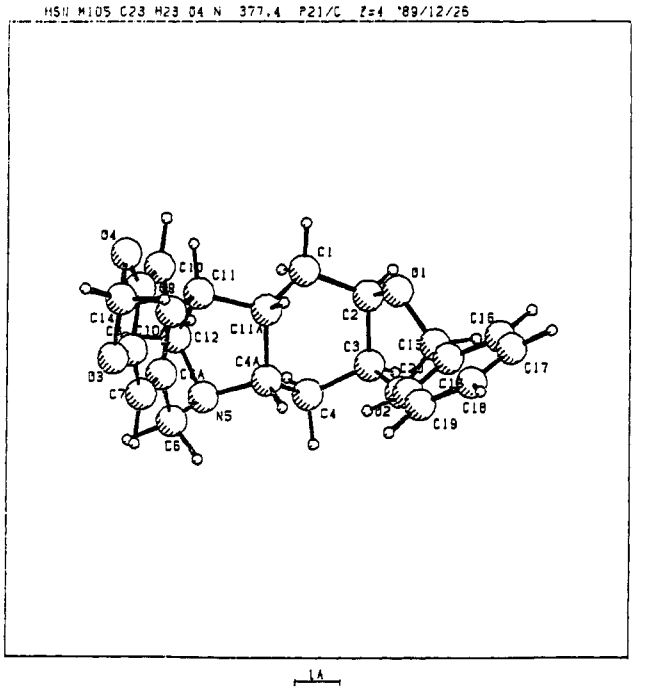
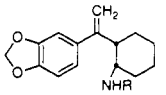



**Figure 2.** X-ray structure of (±)-montanine (**1**).

Reductive cleavage of acetal **22** with diisobutylaluminum hydride (DIBAH)[14] in toluene afforded desired compounds **23a** and **23b** in 75% and 22% yields, respectively.[15] The structures of **23a** and **23b** were determined on the basis of the two-dimensional $^1$H NMR spectra (H–H COSY) of the corresponding acetates **24a** and **24b**.

**Total Synthesis of (±)-Coccinine (2).** We planned to introduce a double bond between C-1 and C-11a in **23a** via a 2-oxo compound because, after introduction of the double bond, the oxo group could be converted to a methoxyl group. Thus, Jones oxidation of **23a** in the usual manner afforded **25** in 59% yield (Scheme V). For insertion of the desired double bond, phenylselenenylation of **25** and subsequent oxidative elimination were tried. Unfortunately, when **25** was treated with base (LDA, NaH, or *t*-BuOK) and then with phenylselenenyl chloride (PhSeCl), complex mixtures were formed in all cases. However, oxidation of **25** with iodobenzene diacetate [PhI(OAc)$_2$][16] in the presence of potassium hydroxide in methanol (MeOH) caused only epimerization of the benzyloxy group at C-3. After fruitless attempts to insert a double bond, oxidation of **25** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[17] in the presence of sodium hydrogen phosphate in refluxing dioxane gave desired enone **26** in 26% yield along with **25** (15%). The reaction of **26** with trimethyl orthoformate in the presence of acid furnished dimethyl acetal **27** in quantitative yield. Reductive cleavage of **27** with DIBAH in toluene afforded **28** as a

(12) The $^1$H NMR spectrum of tosylamide (**A**)[9a] bearing no vicinal acetoxy groups shows signals due to aromatic protons at $\delta$ 6.27–6.40 (3 H, m), whereas the aromatic protons of mesylamide (**B**)[9a] and *tert*-butylcarbamate (**C**)[9a] resonate at $\delta$ 6.68–6.90 (3 H, m) and 6.70 (3 H, s). On the basis of these findings, the formation of a charge-transfer complex between two aromatic rings in **12** was deduced.




A R = Ts
B R = Ms
C R = $CO_2t$-Bu

(13) Ozrazi, O. O.; Corral, R. A.; Giaccio, H. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1977.

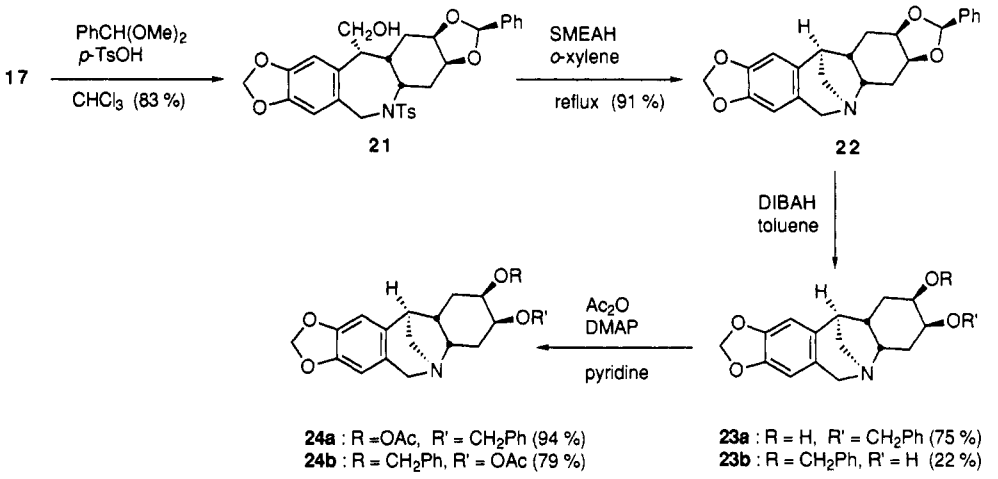
(14) Takano, S.; Akiyama, M.; Sato, S.; Ogasawara, K. *Chem. Lett.* **1983**, 1593.

(15) The reduction of **22** with $LiAlH_4$–$AlCl_3$[29] afforded **23a** and **23b** in 21% and 65% yields, respectively.

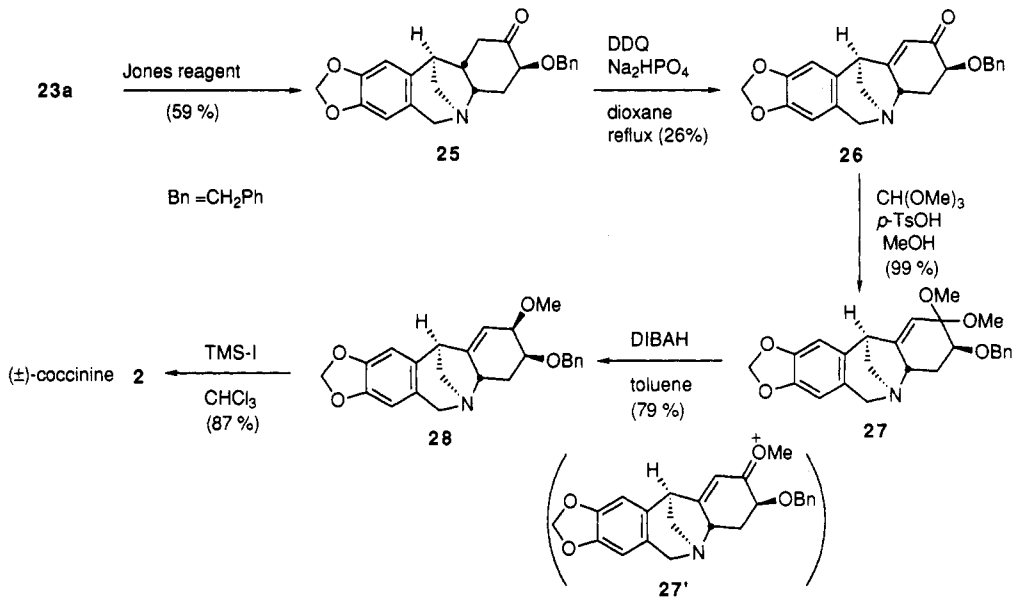
(16) Moriarty, R. M.; Hu, H.; Gupta, S. C. *Tetrahedron Lett.* **1981**, *22*, 1283.

(17) Zderic, J. A.; Carpio, H.; Limon, D. C. *J. Org. Chem.* **1962**, *27*, 1125.

**Scheme IV**




**Scheme V**



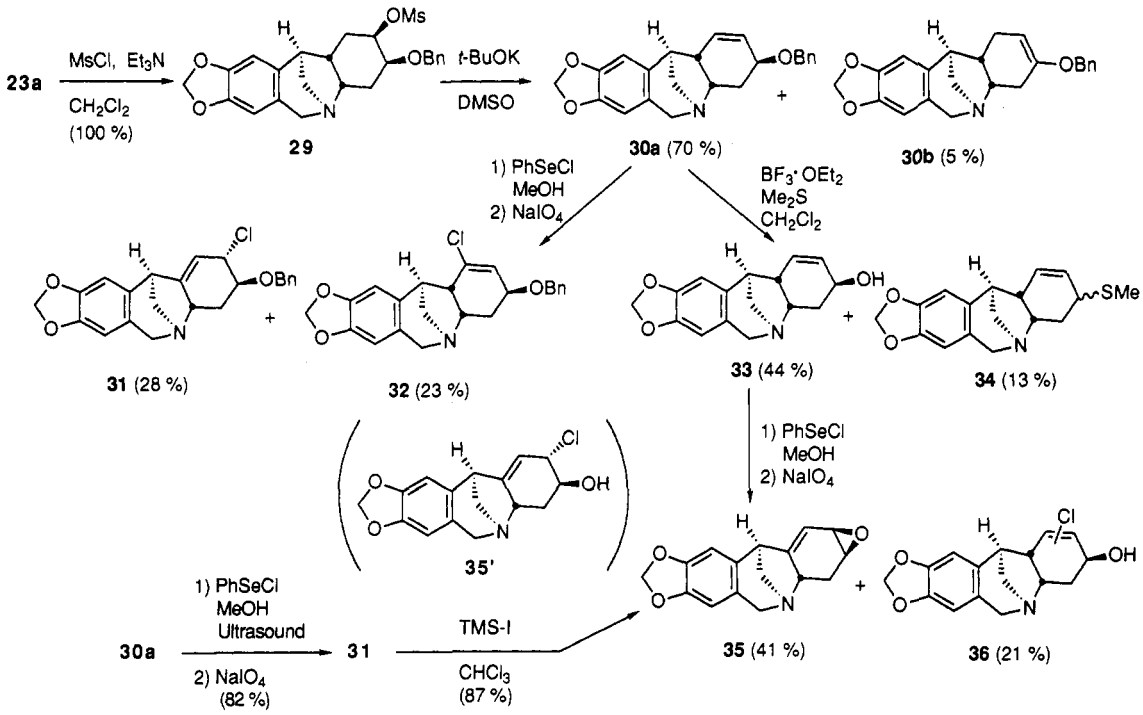

single isomer in 79% yield. Debenzylation of **28** with iodotrimethylsilane (TMS-I)[18] gave (±)-coccinine (**2**) in 87% yield. Mass spectral data of **2** were identical with those reported in the literature.[19] The fact that **28** was generated as a single isomer could be explained by considering that, during the reaction of **27**, oxonium ion **27'** was generated and then reduced with DIBAH from the less hindered $\alpha$-face.

**Total Synthesis of (±)-Montanine (1), (±)-Coccinine (2), (±)-*O*-Acetylmontanine (3), and (±)-Pancracine (4).** Since reductive cleavage of **27** did not give rise to the $\beta$ stereoisomer of **28**, which is a precursor to montanine (**1**), synthesis of an alternative key intermediate was required. For this purpose, introduction of methoxyl and phenylselenenyl groups on the C ring of **30a** followed by oxidative elimination was planned. Thus, mesylation of alcohol **23a** with mesyl chloride in the presence of triethylamine in $CH_2Cl_2$ gave **29** in quantitative yield. Treatment of **29** with potassium *tert*-butoxide in dimethyl sulfoxide afforded olefins **30a** (70%) and **30b** (5%)[20] (Scheme VI).

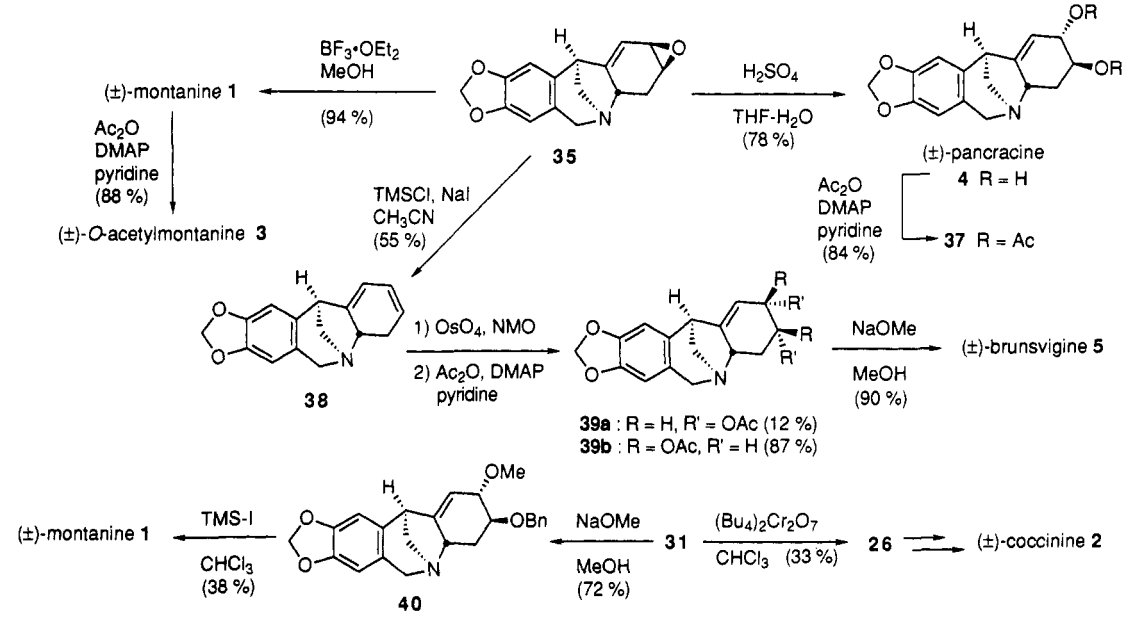
Unexpectedly, reaction of **30a** with PhSeCl did not proceed at all in either MeOH,[21] acetic acid, and potassium acetate[21] or acetonitrile ($CH_3CN$)–$H_2O$[22] at room temperature. Interestingly, allylic chloride **31** (28%) and vinylic chloride **32** (23%), bearing chloro instead of methoxyl groups, were obtained by treatment of **30a** with PhSeCl[23] in refluxing MeOH followed by oxidation with sodium periodate ($NaIO_4$). The structure of **32** was determined by the presence of an NOE between C-2 and C-3 hydrogens in the $^1H$ NMR (500-MHz) spectrum. Since the bulky benzyloxy group was thought to retard the reaction of **30a**, debenzylation was performed. Reaction of **30a** with boron trifluoride etherate ($BF_3$·$Et_2O$) and dimethyl sulfide[24] gave an allylic alcohol **33** (44%) along with methyl sulfide **34** (13%) as byproduct. However, the similar reaction of **33** with PhSeCl in MeOH at room temperature required a prolonged reaction time (3 days), and oxidation with $NaIO_4$ afforded unexpected allylic epoxide **35** and vinylic chloride **36** in 41% and 21% yields, respectively. Because **35** was

(18) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761.
(19) Duffield, A. M.; Apilin, R. T.; Budzikiewicz, H.; Djerassi, C.; Murphy, C. F.; Wildman, W. C. *J. Am. Chem. Soc.* **1965**, *87*, 4902.
(20) Dehydromesylation of **29** with DBU in refluxing *o*-xylene for 2.5 h furnished **30a** and **30b** in 33% and 45% yields, respectively.
(21) Sharpless, K. B.; Lauer, R. F. *J. Org. Chem.* **1974**, *39*, 429.
(22) Toshimitsu, A.; Aoki, T.; Owada, H.; Uemura, S.; Okano, M. *J. Chem. Soc., Chem. Commun.* **1980**, 412.
(23) For regio- and stereoselectivity of the addition of phenylselenenyl chloride to allylic alcohols: Liotta, D.; Zima, G.; Saindane, M. *J. Org. Chem.* **1982**, *47*, 1258.
(24) Fuji, K.; Kawabata, T.; Fujita, E. *Chem. Pharm. Bull.* **1980**, *28*, 3662.

**Scheme VI**




**Scheme VII**




obtained from **33**, it was suggested that debenzylation of **31** might give rise spontaneously to allylic epoxide **35** via allylic chloride **35'**. In addition, since allylic epoxide **35** would be a potent precursor to montamine (**1**) and pancracine (**4**), chlorophenylselenylation of **30a** was reexamined to improve the yield of **31**. After several reaction conditions were explored, the use of dimethylformamide as co-solvent in MeOH was found to give **31** in 50% yield. Interestingly, **31** was obtained even in MeOH, in 82% yield when the reaction was carried out at 15–20 °C under ultrasonication.[25] Debenzylation of **31** with TMS-I gave **35** in 87% yield, as expected. Thus, the overall yield of **35** from **30a** was increased to 73%.

Finally, methanolysis of **35** in MeOH containing $BF_3$·$Et_2O$ afforded (±)-montanine (**1**) in 94% yield (Scheme VII). Mass spectral data of **1** were identical with those reported in the literature.[19] Furthermore, the structure of (±)-**1** was confirmed by X-ray crystallographic analysis (Figure 3). (±)-*O*-Acetylmontanine (**3**) was also obtained in 88% yield by acetylation of (±)-montanine (**1**).

If allylic chloride **31** could be converted to the β-methoxide, synthesis of (±)-**2** might be possible. However, reaction of **31** with sodium methoxide (NaOMe) afforded α-methoxide **40** exclusively. The structure was confirmed by conversion of **40** to (±)-montanine (**1**) in a manner similar to that described for **28**. This outcome could be explained by considering that substitution occurred from the less hindered α-face by means of an $S_N1$-type reaction. Since direct displacement of the α-chloro group with

(25) For recent reviews on the application of ultrasound to organic synthesis, see: (a) Lindley, L.; Mason, T. J. *Chem. Soc. Rev.* **1987**, *16*, 273. (b) Subclick, K. S. In *Modern Synthetic Methods 1986*; Scheffold, R., Ed.; Springer-Verlag: Berlin, 1986; pp1–60.

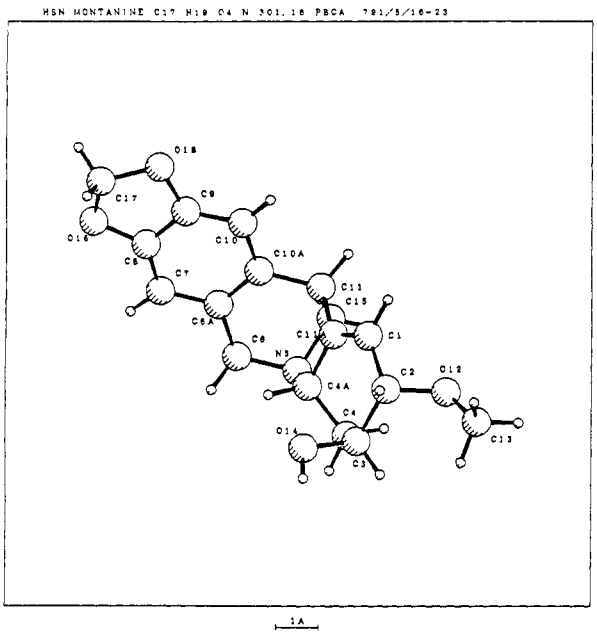


Figure 3.

NaOMe to yield the β-methoxyl group was unsuccessful, **31** was transformed to enone **26**, which was converted to (±)-coccinine (**2**). Oxidation of **31** with bis(tetrabutylammonium) dichromate[26] in boiling chloroform gave enone **26** in 31% yield together with unchanged **31** (17%). Thus, synthesis of (±)-coccinine (**2**) was also achieved via allylic chloride **31**.

In addition, (±)-pancracine (**4**) was synthesized in 78% yield by treatment of **35** with acid. The structure of **4** was determined by its conversion to diacetylpancracine (**37**). Spectral data ($^1$H NMR, MS) of **37** were identical with those reported in the literature.[27]

Since montanine (**1**) had been converted to manthine (**6**) by Wildman et al.,[2b] a formal total synthesis of (±)-manthine (**6**) was also accomplished.

**Total Synthesis of (±)-Brunsvigine (5).** Brunsvigine (**5**), which possesses a 2,3-*cis*-α-diol on ring C, was synthesized as follows (Scheme VII). Deoxygenation of allylic epoxide **35** with chlorotrimethylsilane and sodium iodide[28] in $CH_3CN$ afforded diene **38** in 55% yield. The $^1$H NMR spectrum supported this structure. Osmium oxidation[11] of **38** gave an inseparable mixture of diastereomeric diols, which were separated, after acetylation, to afford α-diacetate **39a** (12%) and β-diacetate **39b** (87%), respectively. $^1$H NMR spectral data of the minor product (**39a**) were identical with those reported in the literature.[5c] Thus, (±)-*O*-acetylbrunsvigine (**39a**) was synthesized from allylic chloride **31**, though in low yield. The reason that the β-diol was predominantly formed over the α-diol was unclear. Finally, hydrolysis of **39a** with NaOMe afforded (±)-brunsvigine (**5**) in 90% yield.

Thus, total syntheses of montanine-type alkaloids **1–5** were accomplished via the allylic chloride **31** using reaction sequences that included cyclization of tosylamide alcohol **21** with SMEAH as the key step.

## Experimental Section

**General.** All melting points were measured on a Büchi or a Yanagimoto (hot plate) melting point apparatus and are uncorrected. Unless otherwise noted, IR spectra were performed with a Hitachi 260-10 spectrometer in $CHCl_3$ solution, and $^1$H NMR spectra were taken with a JEOL JMX-FX100 (100-MHz) or a JEOL GSX-500 (500-MHz) spectrometer in $CDCl_3$ solution with tetramethylsilane as an internal standard. Mass spectra were measured on a Hitachi M-80 or a JEOL JMS D-300 spectrometer. Reactions under ultrasonocation were carried out with an Iuchi ultrasonic cleaner VS-100 instrument. Preparative TLCs were run on Merck 5744 or Merck 7730 plates.

**Materials.** Tetrahydrofuran (THF), ether, dioxane, toluene, and *o*-xylene were distilled from $LiAlH_4$ prior to use. Dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and diisopropylamine were distilled from $CaH_2$ prior to use. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was purchased from Tokyo Kasei Co., Ltd. SMEAH (70% in toluene) was purchased from Nakarai tesque Co., Ltd. $(Bu_4)_2Cr_2O_7$ was prepared according to the reported method.[26]

**(1*R**,2*S**)-2-[3′,4′-(Methylenedioxy)benzoyl]-4-cyclohexenecarboxylic Acid (8).** To an ice-cold, stirred solution of *cis*-cyclohexenedicarboxylic acid anhydride (35.0 g, 0.23 mol) in THF (255 mL) under Ar was added 3,4-(methylenedioxy)-phenylmagnesium bromide (255 mL, 0.236 mol, 0.92 M in THF) over a period of 90 min. After being stirred for another 10 min, the reaction was quenched with $H_2O$ (450 mL) under cooling. The aqueous layer was washed with $CHCl_3$ and acidified with 6 M HCl. The product was taken up in AcOEt. The organic extract was washed with $H_2O$ and dried ($Na_2SO_4$), and the solvent was removed in vacuo to give **8** (60.3 g, 95.6%) as colorless crystals: mp 150–152 °C (AcOEt–hexane); $^1$H NMR (acetone-$d_6$) δ 7.57 (1 H, dd, $J$ = 2, 8 Hz, H-6′), 7.20 (1 H, d, $J$ = 2 Hz, H-2′), 6.90 (1 H, d, $J$ = 8 Hz, H-5′), 6.09 (2 H, s, $OCH_2O$), 5.40–5.80 (2 H, m, olefinic H×2), 4.01 (1 H, dt, $J$ = 4, 6 Hz, H-2), 3.00 (1 H, ddd, $J$ = 2.9, 4, 4,3 Hz, H-1), 2.29–2.79 (4 H, m, H-3×2, H-6×2); IR (KBr) 1705, 1670, 1610 cm$^{-1}$; MS $m/z$ 274 ($M^+$). Anal. Calcd for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 65.72; H, 5.14.

**(1*R**,2*S**)-*N*-(*tert*-Butoxycarbonyl)-2-[3′,4′-(methylenedioxy)benzoyl]-4-cyclohexenylamide (9).** To an ice-cold, stirred solution of carboxylic acid **8** (31.6 g, 0.115 mol) and $Et_3N$ (12.48 g, 0.123 mol) in acetone (250 mL) and $H_2O$ (50 mL) was added dropwise ethyl chloroformate (13.46 g, 0.124 mol). After the reaction mixture was stirred for 0.5 h, a solution of $NaN_3$ (8.48 g, 0.13 mol) in $H_2O$ (100 mL) was added to the mixture, and stirring was continued at the same temperature for 1 h. Then the mixture was extracted with $CHCl_3$, and the extract was washed with 1 M HCl, saturated $NaHCO_3$, and $H_2O$, successively, and dried ($Na_2SO_4$). The solvent was evaporated in vacuo to give an oily residue, which was refluxed in *t*-BuOH (500 mL) for 16 h. Evaporation of the solvent in vacuo afforded **9** (37.36 g, 93.9%): mp 120–121 °C (AcOEt–hexane); $^1$H NMR δ 7.47 (1 H, dd, $J$ = 1.7, 8 Hz, H-6′), 7.34 (1 H, d, $J$ = 1.7 Hz, H-2′), 6.83 (1 H, d, $J$ = 8 Hz, H-5′), 6.02 (2 H, s, $OCH_2O$), 5.46–5.82 (2 H, m, olefinic H×2), 4.90 (1 H, d, $J$ = 12 Hz, NH), 4.04–4.36 (1 H, m, H-2), 3.52–3.83 (1 H, m, H-1), 2.04–2.84 (4 H, m, H-3×2, H-6×2), 1.37 (9 H, s, *t*-Bu); IR (KBr) 3440, 1705, 1670, 1605 cm$^{-1}$; MS $m/z$ 345 ($M^+$). Anal. Calcd for $C_{19}H_{23}NO_5$: C, 66.07; H, 6.71; N, 4.06. Found: C, 66.32; H, 6.62; N, 4.12.

**(1*R**,2*S**)-2-[3′,4′-(Methylenedioxy)benzoyl]-4-cyclohexenyl-*N*-tosylamide (10).** A solution of carbamate **9** (17.68 g, 51.2 mmol) and TFA (40 mL) in $CH_2Cl_2$ (400 mL) was stirred at rt for 1 h. After $H_2O$ was added to the mixture, the mixture was made alkaline with solid $K_2CO_3$. The aqueous layer was extracted with $CHCl_3$. The extract was dried ($K_2CO_3$) and evaporated in vacuo to give an oily residue, which was treated with $Et_3N$ (7.60 g, 75 mmol) and *p*-TsCl (9.53 g, 50 mmol) in $CHCl_3$ (150 mL) at rt for 1 h. The mixture was washed with 3 M HCl and $H_2O$, successively, and dried ($Na_2SO_4$). Removal of the solvent in vacuo gave a crude carbamate, which was subjected to silica gel column chromatography ($CHCl_3$ and 40:1 $CHCl_3$–AcOEt) to afford **10** (14.52 g, 71.3%) as colorless crystals: mp 150 °C (AcOEt–hexane); $^1$H NMR δ 7.58, 7.20 (each 2 H, d, $J$ = 8 Hz, arom H×4), 7.24 (1 H, dd, $J$ = 2, 8 Hz, H-6′), 7.05 (1 H, d, $J$ = 2 Hz, H-2′), 6.74 (1 H, d, $J$ = 8 Hz, H-5′), 6.02 (2 H, s, $OCH_2O$), 5.44–5.76 (2 H, m, olefinic H×2), 5.08 (1 H, d, $J$ = 8 Hz, NH), 3.36–3.87 (2 H, m, H-2, H-1), 2.36 (3 H, s, Me), 2.00–2.72 (4 H, m, H-3×2, H-6×2); IR 3360, 1670, 1600 cm$^{-1}$; MS $m/z$ 399

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($M^+$). Anal. Calcd for $C_{21}H_{21}NO_5S$: C, 63.14; H, 5.30; N, 3.51; S, 8.03. Found: C, 63.03; H, 5.03; N, 3.78; S, 7.88.

**Catalytic Osmium Oxidation of 10.** A mixture of olefin **10** (4.02 g, 10 mmol), *N*-methylmorpholine *N*-oxide[11] (1.24 g, 10.6 mmol), and $OsO_4$ (0.5 mL, 0.2 mmol, 0.4 M in dioxane) in dioxane (40 mL)–$H_2O$ (10 mL) was stirred at rt for 2 h. After the reaction was quenched with 10% $Na_2S_2O_3$, the mixture was extracted with $CHCl_3$. The organic layer was washed with 1 M HCl and $H_2O$, successively, and dried ($Na_2SO_4$). Evaporation of the solvent in vacuo gave diastereomeric diols (4.36 g, 100%), which were treated with $Ac_2O$ (6.16 g, 60 mmol) and DMAP (63 mg, 0.52 mmol) in pyridine (15 mL) at rt for 2 h. After the usual workup, the crude product was purified by alumina column chromatography ($CHCl_3$) to give **11a** (4.82 g, 92.7%) and **11b** (0.264 g, 5.1%). **11a**: mp 254–256 °C (AcOEt–hexane); $^1H$ NMR $\delta$ 7.58, 7.08 (each 2 H, d, $J$ = 8 Hz, arom H×4), 7.26 (1 H, dd, $J$ = 1.4, 8 Hz, H-6′), 7.09 (1 H, d, $J$ = 1.4 Hz, H-2′), 6.76 (1 H, d, $J$ = 8 Hz, H-5′), 6.04 (2 H, s, $OCH_2O$), 4.84–5.32 (3 H, m, NH, H-4, H-5), 3.60–3.88 (2 H, m, H-2, H-1), 2.32 (3 H, s, Me), 2.00, 1.99 (each 3 H, s, OAc×2), 1.64–2.59 (4 H, m, H-3×2, H-6×2); IR 3375, 1740, 1660, 1600 $cm^{-1}$; MS $m/z$ 517 ($M^+$). Anal. Calcd for $C_{25}H_{27}NO_9S$: C, 58.02; H, 5.26; N, 2.71; S, 6.20. Found: C, 58.04; H, 5.40; N, 2.76; S, 6.09. **11b**: mp 230–231 °C (AcOEt–hexane); $^1H$ NMR $\delta$ 7.56, 7.12 (each 2 H, d, $J$ = 8 Hz, arom H×4), 7.21 (1 H, dd, $J$ = 1.4, 8 Hz, H-6′), 7.01 (1 H, dd, $J$ = 1.4, 8 Hz, H-2′), 6.73 (1 H, d, $J$ = 8 Hz, H-5′), 6.03 (2 H, s, $OCH_2O$), 5.56 (1 H, d, $J$ = 10 Hz, NH), 4.84–5.12 (2 H, m, H-4, H-5), 3.52–3.88 (1 H, m), 3.36 (1 H, q, $J$ = 5.2 Hz), 2.35 (3 H, s, Me), 2.04, 1.90 (each 3 H, s, OAc×2), 1.64–2.70 (4 H, m, H-3×2, H-6×2); IR 3370, 1740, 1670, 1605 $cm^{-1}$; MS $m/z$ 517 ($M^+$). Anal. Calcd for $C_{25}H_{27}NO_9S$: C, 58.02; H, 5.26; N, 2.71; S, 6.20. Found: C, 58.19; H, 5.45; N, 2.46; S, 6.41.

**(1*R**,2*R**,4*S**,5*R**)-4,5-Diacetoxy-2-[1′-[3″,4″-(methylenedioxy)phenyl]vinyl]-1-cyclohexyl-*N*-tosylamide (12).** A mixture of $PPh_3MeBr$ (11.90 g, 33.3 mmol) and *t*-BuOK (3.70 g, 33 mmol) in THF (150 mL) under Ar was stirred at rt for 0.5 h. Ketone **11a** (3.1014 g, 6.0 mmol) was added to the mixture in one portion. After being stirred at rt for 2 h, the reaction was quenched with $H_2O$. Then the mixture was extracted with $CHCl_3$. The extract was dried ($Na_2SO_4$) and evaporated in vacuo to give a crude product, which was purified by silica gel column chromatography (1:1 AcOEt–hexane) to give **12** (2.2075 g, 71.4%): mp 163–164.5 °C (AcOEt–hexane); $^1H$ NMR $\delta$ 7.48, 7.11 (each 2 H, d, $J$ = 8 Hz, arom H×4), 6.40–6.56 (3 H, m, arom H×3), 5.96, 5.92 (each 1 H, d, $J$ = 1 Hz, $OCH_2O$), 5.38–5.56 (1 H, m, NH), 5.28, 4.94 (each 1 H, s, olefinic H×2), 5.12 (2 H, ddd, $J$ = 2.4, 4, 12 Hz, H-4, H-5), 2.96–3.30 (2 H, m, H-1, H-2), 2.38 (3 H, s, Me), 2.11, 1.97 (each 3 H, s, OAc×2), 1.52–2.14 (4 H, m, H-3×2, H-6×2); IR 3300, 1735, 1600 $cm^{-1}$; MS $m/z$ 515 ($M^+$). Anal. Calcd for $C_{26}H_{29}NO_8S$: C, 60.57; H, 5.67; N, 2.72; S, 6.22. Found: C, 60.84; H, 5.81; N, 2.73; S, 6.19.

**(1*R**,1′*S**,2*R**,4*S**,5*R**)-4,5-Diacetoxy-2-[2′-hydroxy-1′-[3″,4″-(methylenedioxy)phenyl]ethyl]-1-cyclohexyl-*N*-tosylamide (13).** To an ice-cold, stirred solution of olefin **12** (3.53 g, 6.85 mmol) in THF (60 mL) was added 1 M $BH_3$-THF (13.4 mL, 13.4 mmol) over a period of 15 min. After the reaction mixture was stirred at the same temperature for 4 h, $H_2O$ (5 mL) was added. Then the mixture was treated with 3 M NaOH (3.4 mL) and 30% $H_2O_2$ (3.4 mL) at rt for 40 min and extracted with $CHCl_3$. The solvent was washed with brine and dried ($Na_2SO_4$). Removal of the solvent in vacuo produced **13** (3.65 g, 100%): mp 168–169 °C (AcOEt–hexane); $^1H$ NMR $\delta$ 7.80, 7.30 (each 2 H, d, $J$ = 8 Hz, arom H×4), 6.40–6.76 (3 H, m, arom H×3), 5.89 (2 H, s, $OCH_2O$), 5.76 (1 H, d, $J$ = 10 Hz, NH), 4.80–5.20 (2 H, m, H-4, H-5), 3.84–4.10 (1 H, m, H-1), 3.69 (2 H, d, H-2′), 2.52–2.82 (1 H, m, H-2), 2.41 (3 H, s, Me), 2.00, 1.92 (each 3 H, s, OAc×2), 1.22–2.28 (4 H, m, H-3×2, H-6×2); IR 3200–3600, 1735, 1600 $cm^{-1}$; MS $m/z$ 533 ($M^+$). Anal. Calcd for $C_{26}H_{31}NO_9S$: C, 58.52; H, 5.86; N, 2.63; S, 6.01. Found: C, 58.60; H, 5.91; N, 2.60; S, 5.71.

**Octahydroindoline (14).** A mixture of tosylamide alcohol **13** (266.8 mg, 0.5 mmol) and *p*-TsCl (201.9 mg, 1.06 mmol) in pyridine (2 mL) was refluxed for 10 min. After extraction with $CHCl_3$, the extract was washed with 3 M HCl and brine, successively, dried ($Na_2SO_4$), and evaporated. Silica gel chromatography (20:1 $CHCl_3$–AcOEt) of the residue gave **14** (212.2 mg, 82.3%): mp 218–219 °C (AcOEt–hexane); $^1H$ NMR (500 MHz) $\delta$ 7.76, 7.37 (each 2 H, d, $J$ = 8 Hz, arom H×4), 6.70 (1 H, d, $J$ = 8 Hz, arom H), 6.50 (1 H, dd, $J$ = 2, 8 Hz, arom H), 6.36 (1 H, d, $J$ = 2 Hz, arom H), 5.93, 5.92 (each 1 H, d, $J$ = 1.5 Hz, $OCH_2O$), 5.33 (1 H, brt, $J$ = 3 Hz, H-6), 4.95 (1 H, ddd, $J$ = 2.5, 5, 11.8 Hz, H-5), 4.13 (1 H, dt, $J$ = 7, 10.5 Hz, H-7a), 3.75 (1 H, dd, $J$ = 7, 9.5 Hz, H-2), 3.24 (1 H, ddd, $J$ = 7.5, 9.5, 11.4 Hz, H-3), 3.17 (1 H, t, $J$ = 9.5 Hz, H-2), 2.48 (3 H, s, Me), 2.37 (1 H, dt, $J$ = 5, 14.5 Hz, H-7), 2.12 (3 H, s, OAc), 2.03–2.10 (1 H, m, H-3a), 1.95 (3 H, s, OAc), 1.80–1.92 (2 H, m, H-4, H-7), 1.49–1.57 (1 H, m, H-4); IR 1740 $cm^{-1}$; MS $m/z$ 515 ($M^+$). Anal. Calcd for $C_{26}H_{29}NO_8S$: C, 60.57; H, 5.67; N, 2.72; S, 6.22. Found: C, 60.47; H, 5.80; N, 2.74; S, 6.35.

**(1*R**,1′*S**,2*R**,4*S**,5*R**)-2-[2′-Acetoxy-1′-[3″,4″-(methylenedioxy)phenyl]ethyl]-4,5-diacetoxy-1-cyclohexyl-*N*-tosylamide (15).** A mixture of tosylamide alcohol **13** (3.1505 g, 5.9 mmol) and $Ac_2O$ (6 mL) in pyridine (15 mL) was stirred at rt for 1 h. Extraction with $CHCl_3$ followed by usual workup of the mixture gave **15** (3.9366, 100%): mp 159–160 °C ($CHCl_3$-hexane); $^1H$ NMR $\delta$ 7.80, 7.30 (each 2 H, d, $J$ = 8 Hz, arom H×4), 6.38–6.72 (3 H, m, arom H×3), 5.89 (2 H, s, $OCH_2O$), 5.72 (1 H, d, $J$ = 8 Hz, NH), 4.80–5.20 (2 H, m, H-4, H-5), 3.72–4.26 (3 H, m, H-1, H′-2×2), 2.62–2.93 (1 H, m, H-2), 2.41 (3 H, s, Me), 2.01, 1.94, 1.93 (each 3 H, s, OAc×3), 1.56–1.82, 1.22–1.48 (each 2 H, m, H-3×2 or H-6×2); IR 3270–3600, 1735, 1600 $cm^{-1}$; MS $m/z$ 575 ($M^+$). Anal. Calcd for $C_{28}H_{33}NO_{10}S$: C, 58.42; H, 5.78; N, 2.43; S, 5.57. Found: C, 58.62; H, 5.51; N, 2.49; S, 5.87.

**(2*S**,3*R**,4a*R**,11*S**,11a*R**)-2,3-Diacetoxy-11-(acetoxymethyl)-8,9-(methylenedioxy)-5-tosylmorphanthridine (16).** A solution of methanesulfonic acid (1.1532 g, 12 mmol)[13] in 1,2-dichloroethane (3 mL) was added dropwise to a stirred suspension of tosylamide acetate **15** (1.1505 g, 2.9 mmol), paraformaldehyde (0.1826 g, 6 mmol), and $Ac_2O$ (0.4134 g, 4 mmol) in 1,2-dichloroethane (10 mL), and stirring was continued at rt for 2 h. Then the reaction was quenched with $H_2O$. After separation of the organic layer, the aqueous layer was extracted with $CHCl_3$. The combined extracts were washed with saturated $NaHCO_3$ and brine, successively, and dried ($Na_2SO_4$). The solvent was evaporated in vacuo to give an oily residue, which was purified by silica gel column chromatography ($CHCl_3$ and 40:1 $CHCl_3$–AcOEt) to produce **16** (0.9462 g, 80.6%): mp 168.5 °C (AcOEt–hexane); $^1H$ NMR $\delta$ 7.66, 7.26 (each 2 H, d, $J$ = 8 Hz, arom H×4), 6.61, 6.60 (each 1 H, s, arom H×2), 5.94 (2 H, s, $OCH_2O$), 4.88–5.10, 4.64–4.88 (each 1 H, m, H-2 or H-3), 3.96–4.60 (4 H, m, H-6×2, $CH_2OAc$), 3.04–3.40 (1 H, m, CHNTs), 2.32–2.68 (1 H, m, H-11), 2.42 (3 H, s, Me), 2.02, 2.01, 2.00 (each 3 H, s, OAc×3), 1.32–1.82 (5 H, m, H-1×2, H-4×2, H-11a); IR 1735 $cm^{-1}$; MS $m/z$ 587 ($M^+$). Anal. Calcd for $C_{29}H_{33}NO_{10}S$: C, 59.27; H, 5.66; N, 2.38; S, 5.46. Found: C, 59.29; H, 5.78; N, 2.26; S, 5.48.

**(2*S**,3*R**,4a*R**,11*S**,11a*R**)-2,3-Dihydroxy-11-(hydroxymethyl)-8,9-(methylenedioxy)-5-tosylmorphanthridine (17).** A mixture of tosylamide acetate **16** (2.9259 g, 4.98 mmol) and NaOMe (0.9321 g, 16.56 mmol) in MeOH (30 mL) was stirred at rt for 20 min. Extraction with $CHCl_3$ followed by the usual workup of the mixture gave **17** (2.2978 g, 100%): mp 188–189 °C (acetone–hexane); $^1H$ NMR (pyridine-$d_5$) $\delta$ 7.94, 7.20 (each 2 H, d, $J$ = 8 Hz, arom H×4), 7.03, 7.00 (each 1 H, s, arom H×2), 5.96 (2 H, s, $OCH_2O$), 5.06 (1 H, d, $J$ = 16 Hz, H-6), 3.96–4.68 (5 H, m, $CH_2OH$, H-2, H-3, H-6), 3.44–3.72 (1 H, m, H-4a), 3.06–3.38 (1 H, m, H-11), 1.40–2.67 (5 H, m, H-1×2, H-4×2, H-11a); IR (KBr) 3100–3600 $cm^{-1}$; MS $m/z$ 461 ($M^+$). Anal. Calcd for $C_{23}H_{27}NO_7S$: C, 59.86; H, 5.90; N, 3.03; S, 6.95. Found: C, 59.94; H, 5.98; N, 3.03; S, 6.91.

**(2*S**,3*R**,4a*R**,11*S**,11a*R**)-8,9-(Methylenedioxy)-5,11-methanomorphanthridine-2,3-diol (18).** A mixture of triol **17** (92.7 mg, 0.2 mmol) and SMEAH (0.5 mL, 1.6 mmol) in toluene (2 mL) under Ar was refluxed for 7 h. Then $H_2O$ was added to the ice-cold mixture and the aqueous layer was extracted with $CHCl_3$. The organic extract was washed with $H_2O$ and dried ($K_2CO_3$). Removal of the solvent in vacuo gave a crude product, which was subjected to silica gel column chromatography (10:1 $CHCl_3$–MeOH) to afford **18** (14.5 mg, 30.0%): mp 202–203 °C (AcOEt–hexane); $^1H$ NMR (pyridine-$d_6$) $\delta$ 6.56, 6.32 (each 1 H, s, arom H×2), 5.93 (2 H, s, $OCH_2O$), 4.25, 3.70 (each 1 H, d, $J$ = 17.1 Hz, H-6×2), 4.12–4.36 (2 H, m, H-2, H-3), 3.38–3.68 (1 H, m, H-4a), 3.14 (1 H, dd, $J$ = 2.6, 11.2 Hz, H-12), 2.70–2.96 (2 H, m, H-11a, H-12), 2.36–2.54 (1 H, m, H-11), 1.42–2.28 (4 H, m, H-1×2, H-4×2); IR (KBr) 3300–3550, 1500, 1480 $cm^{-1}$; MS $m/z$

289 ($M^+$). Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.22; H, 6.80; N, 4.76.

**(2*S**,3*R**,4a*R**,11*S**,11a*R**)-2,3-*O*-Isopropylidene-2,3-dihydroxy-8,9-(methylenedioxy)-5-tosylmorphanthridine (19).** A solution of triol **17** (185.3 mg, 0.4 mmol), 2,2-dimethoxypropane (145.9 mg, 1.4 mmol), and *p*-TsOH·$H_2O$ (7.6 mg, 0.04 mmol) in $CHCl_3$ (5 mL) was stirred at rt for 3 h. The mixture was washed with saturated $NaHCO_3$ and brine, successively, and dried ($Na_2SO_4$). The solvent was removed in vacuo to give a residue, which was purified by silica gel preparative TLC (15:1 $CHCl_3$–MeOH) to give **19** (196.9 mg, 97.7%): mp 235 °C (AcOEt–hexane); $^1H$ NMR $\delta$ 7.73, 7.29 (each 2 H, d, $J$ = 8 Hz, arom H×4), 6.62, 6.48 (each 1 H, s, arom H×2), 5.88, 5.90 (each 1 H, d, $J$ = 1.6 Hz, $OCH_2O$), 5.17, 3.96 (1 H, d, $J$ = 15.4 Hz, H-6), 4.70 (1 H, ddd, $J$ = 5.1, 10, 12 Hz, H-4a), 3.64–4.30 (4 H, m, $CH_2OH$, H-2, H-3), 2.46–2.80 (1 H, m, H-11), 2.42 (3 H, s, Me), 1.76 (1 H, ddd, $J$ = 3.2, 6.4, 14 Hz, H-11a), 1.59, 1.57 (each 3 H, s, Me×2), 0.84–1.16 (4 H, m); IR 3200–3650 $cm^{-1}$; MS $m/z$ 501 ($M^+$). Anal. Calcd for $C_{26}H_{31}NO_7S$: C, 62.26; H, 6.23; N, 2.79; S, 6.39. Found: C, 62.51; H, 6.38; N, 2.78; S, 6.49.

**(2*S**,3*R**,4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-*syn*-2,3-*O*-Isopropylidene-2,3-dihydroxy-8,9-(methylenedioxy)methanomorphanthridine (20).** A mixture of tosylamide alcohol **19** (1.0018 g, 2 mmol) and SMEAH (4 mL, 13.2 mmol) in toluene (6 mL) under Ar was refluxed for 3 h. The reaction was quenched with 3 N NaOH with cooling. The mixture was extracted with $CHCl_3$. A workup of the organic extract similar to that described for **17** gave a solid, which was purified by alumina column chromatography ($CHCl_3$ and 30:1 $CHCl_3$–MeOH) to give **20** (575.3 mg, 87.4%): mp 145 °C (acetone); $^1H$ NMR $\delta$ 6.44, 6.42 (each 1 H, s, arom H×2), 5.84 (2 H, s, $OCH_2O$), 4.20–4.52 (2 H, m, H-2, H-3), 4.28, 3.72 (each 1 H, d, $J$ = 17 Hz, H-6×2), 3.26 (1 H, dt, $J$ = 7, 12 Hz, H-4a), 3.04 (1 H, dd, $J$ = 2.6, 11.4 Hz, H-12), 2.88 (1 H, d, $J$ = 11.4 Hz, H-12), 2.53 (1 H, d, $J$ = 2.6 Hz, H-11), 1.72–2.63 (5 H, m), 1.37, 1.28 (each 3 H, s, Me); IR 1500, 1480 $cm^{-1}$; MS $m/z$ 329 ($M^+$). Anal. Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.38; H, 7.16; N, 4.24.

**(2*S**,3*R**,4a*R**,11*S**,11a*R**)-2,3-*O*-Benzylidene-2,3-dihydroxy-11-(hydroxymethyl)-8,9-(methylenedioxy)-5-tosylmorphanthridine (21).** A solution of triol **17** (2.2397 g, 4.86 mmol), benzaldehyde dimethyl acetal (890 mg, 5.85 mmol), and *p*-TsOH·$H_2O$ (49.3 mg, 0.26 mmol) in $CHCl_3$ (20 mL) was stirred at rt for 80 min. Usual workup of the mixture gave an oily residue, which was subjected to silica gel column chromatography ($CHCl_3$ and 100:1 $CHCl_3$–MeOH) to produce **21** (2.2009 g, 82.5%): mp 235–237 °C (AcOEt–hexane); $^1H$ NMR $\delta$ 7.52, 7.12 (each 2 H, d, $J$ = 8 Hz, arom H×4), 7.20–7.72 (5 H, m, arom H×5), 6.63, 6.49 (each 1 H, s, arom H×2), 5.96, 5.88 (each 1 H, d, $J$ = 2 Hz, $OCH_2O$), 5.62 (1 H, s, CHAr), 5.23 (1 H, d, $J$ = 16 Hz, H-6), 4.83 (1 H, dt, $J$ = 4.8, 11.2 Hz, H-2), 3.60–4.32 (5 H, m, $CH_2OH$, H-3, H-4a, H-6), 2.36–2.96 (1 H, m, ArCH), 2.35 (3 H, s, Me), 1.92 (1 H, ddd, $J$ = 3.2, 6, 14.3 Hz, H-4), 0.88–1.36 (4 H, m, H-11a, H-1×2, H-4); IR 1600, 1490 $cm^{-1}$; MS $m/z$ 549 ($M^+$). Anal. Calcd for $C_{30}H_{31}NO_7S$: C, 65.56; H, 5.69; N, 2.55; S, 5.83. Found: C, 65.66; H, 5.82; N, 2.49; S, 5.86.

**(2*S**,3*R**,4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-*syn*-2,3-*O*-Benzylidene-2,3-dihydroxy-8,9-(methylenedioxy)-5,11-methanomorphanthridine (22).** A mixture of tosylamide alcohol **21** (275 mg, 0.5 mmol) and SMEAH (1 mL, 3.4 mmol) on *o*-xylene (2 mL) under Ar was refluxed for 35 min. After addition of saturated $Na_2SO_4$ with cooling, the precipitate was removed by suction filtration through a short pad of Celite 545. The filtrate was dried ($K_2CO_3$) and evaporated in vacuo to give a residue, which was purified by silica gel column chromatography (20:1 $CHCl_3$–MeOH) to afford **23** (171.2 mg, 90.7%): mp 180–181 °C (acetone); $^1H$ NMR (500 MHz) $\delta$ 7.40–7.44 (2 H, m, arom H×2), 7.32–7.36 (3 H, m, arom H×3), 6.48, 6.46 (each 1 H, s, arom H×2), 5.90, 5.87 (each 1 H, d, $J$ = 1.5 Hz, $OCH_2O$), 5.61 (1 H, s, CHAr), 4.45, 4.38 (each 1 H, dt, $J$ = 2.5, 8.5 Hz, H-2, H-3), 4.31, 3.77 (each 1 H, d, $J$ = 17 Hz, H-6×2), 3.38 (1 H, dt, $J$ = 7, 12 Hz, H-4a), 3.08 (1 H, dd, $J$ = 3, 12 Hz, H-12), 2.94 (1 H, d, $J$ = 12 Hz, H-12), 2.68 (1 H, ddd, $J$ = 5.5, 7.5, 13.5 Hz, H-11a), 2.57 (1 H, d, $J$ = 3 Hz, H-11), 2.47 (1 H, ddd, $J$ = 3, 6.5, 14.5 Hz, H-4), 2.13 (1 H, ddd, $J$ = 3, 5.5, 14.5 Hz, H-1), 1.44 (1 H, dt, $J$ = 2.5, 14.5 Hz, H-4), 1.43 (1 H, dt, $J$ = 2.5, 14.5 Hz, H-1); IR 1500, 1480 $cm^{-1}$; MS $m/z$ 377 ($M^+$). Anal. Calcd for $C_{23}H_{23}NO_4$: C, 73.19; H, 6.14; N, 3.71. Found: C, 73.40; H, 6.17; N, 3.72.

**Table I. Crystal Data and Summaries of Structure Determination**

| | | |
|---|---|---|
| compd name | benzylidene acetal **22** | (±)-montanine (1) |
| formula MW | $C_{23}H_{23}NO_4$, 377.4 | $C_{17}H_{19}NO_4$, 301.3 |
| crystal system | monoclinic | orthorhombic |
| space group, $Z$ | $P2_{1/c}$, 4 | $Pbca$, 8 |
| lattice constant $a$ (Å) | 10.473 (6) | 15.444 (9) |
| $b$ (Å) | 19.156 (10) | 17.863 (10) |
| $c$ (Å) | 9.868 (6) | 11.0347 (7) |
| $\beta$ (deg) | 107.62 (6) | |
| $V$ (Å$^3$) | 1887 | 3044 |
| $D_{calcd}$ (g cm$^{-1}$) | 1.329 | 1.315 |
| $m$ for Cu K$\alpha$ (cm$^{-1}$) | 7.0 | 7.3 |
| crystal size (mm$^3$) | 0.2 × 0.3 × 0.5 | 0.3 × 0.1 × 0.4 |
| color, habit | colorless prism | colorless plate |
| obsd $2\theta$ range (deg) | 6–156 | 6–156 |
| no. of reflns | | |
| obsd as $I > 2\sigma(I)$ | 3256 | 2539 |
| used for structure determination | 3065 | 2507 |
| symmetry equiv | 191 | 32 |
| $R_f$ for the above reflns | 0.02 | 0.02 |
| refinement by | block-diagonal-matrix least-squares | |
| final $R$ value | 0.053 | 0.066 |
| refined atom, anisotropic | 28 C, N, O | 22 C, N, O |
| isotropic | 23 H | 19 H |

**X-ray Crystallographic Analysis.** The X-ray studies of benzylidene acetal **22** and (±)-montanine (**1**) were carried out with a Philip PW 1100 diffractometer. The intensity data were obtained using Cu K$\alpha$ radiation monochromated by the use of a graphite plate. Crystal data and the course of the structure determination are summarized in Table I, and the PLUTO[30] drawings of both structures are given in Figures 2 and 3.

**Acetalization of Diol (18).** A solution of diol **18** (28.9 mg, 0.1 mmol), benzaldehyde dimethyl acetal (24.5 mg, 0.16 mmol), and *p*-TsOH·$H_2O$ (22.1 mg, 0.116 mmol) in $CHCl_3$ (1.5 mL) was stirred at rt for 4 h. Then the mixture was washed with brine, and the solvent was dried ($K_2CO_3$). Removal of the solvent in vacuo gave an oily residue which was subjected to silica gel column chromatography ($CHCl_3$ and 10:1 $CHCl_3$–MeOH) to give **22** (37.1 mg, 98.4%), $^1H$ NMR and IR spectra of which were identical to those of an authentic sample obtained from **21**.

**(2*S**,3*R**,4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-*syn*-3-(Benzyloxy)-2-hydroxy-8,9-(methylenedioxy)-5,11-methanomorphanthridine (23a) and (2*S**,3*R**,4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-*syn*-2-(Benzyloxy)-3-hydroxy-8,9-(methylenedioxy)-5,11-methanomorphanthridine (23b).** A mixture of acetal **22** (127.8 mg, 0.34 mmol) and DIBAH (2 mL, 2 M in toluene) in toluene (2 mL) was stirred at rt for 2 h under Ar. The reaction was quenched with $H_2O$, and the precipitate was filtered through a short pad of Celite 545. The filtrate was dried ($K_2CO_3$), and the solvent was removed in vacuo to afford a residue, silica gel column chromatography (30:1 $CHCl_3$–MeOH) of which afforded **23a** (95.8 mg, 74.6%) and **23b** (28.6 mg, 22.3%). **23a**: mp 161–162 °C (AcOEt–hexane); $^1H$ NMR $\delta$ 7.28 (5 H, s, arom H×5), 6.48, 6.42 (each 1 H, s, arom H×2), 5.85 (2 H, s, $OCH_2O$), 4.64, 4.50 (each 1 H, d, $J$ = 11.6 Hz, $CH_2Ph$), 4.28, 3.70 (each 1 H, d, $J$ = 16.6 Hz, H-6×2), 3.96–4.12 (1 H, m, H-3), 3.76 (1 H, dt, $J$ = 3.5, 6 Hz, H-2), 2.80–3.40 (3 H, m, H-4a, H-12×2), 2.44–2.76 (2 H, m, H-11, H-11a), 1.50–2.28 (4 H, m, H-1×2, H-4×2); IR 3500, 1500, 1480 $cm^{-1}$; MS $m/z$ 379 ($M^+$). Anal. Calcd for $C_{23}H_{25}NO_4$: C, 72.80; H, 6.64; N, 3.69. Found: C, 73.08; H, 6.82; N, 3.61. **23b**: mp 123–124 °C ($Et_2O$); $^1H$ NMR $\delta$ 7.28 (5 H, s, arom H×5), 6.42, 6.41 (each 1 H, s, arom H×2), 5.84 (2 H, s, $OCH_2O$), 4.64, 4.48 (each 1 H, d, $J$ = 12 Hz, $CH_2Ph$), 4.26, 3.74 (each 1 H, d, $J$ = 17.1 Hz, H-6×2), 4.03 (1 H, dt, $J$ = 2.9, 5.7 Hz, H-2), 3.60–3.80 (1 H, m, H-3), 3.22–3.52 (1 H, m, H-4a), 3.10 (1 H, dd, $J$ = 2, 10 Hz, H-12), 2.51 (1 H, d, $J$ = 2 Hz, H-12), 1.84–2.80 (5 H, m, H-1, H-4×2, H-11, H-11a), 1.40–1.64 (1 H, m, H-1); IR 3525, 1500, 1480

(30) Motherwell, W. D. S.; Clegg, W. PLUTO. A Program for Drawing Molecular and Crystal Structures, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England, 1983.

$cm^{-1}$; MS $m/z$ 379 ($M^+$). Anal. Calcd for $C_{23}H_{25}NO_4$: C, 72.80; H, 6.64; N, 3.69. Found: C, 72.86; H, 6.62; N, 3.75.

**(2*S**,3*R**,4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-*syn*-2-Acetoxy-3-(benzyloxy)-8,9-(methylenedioxy)-5,11-methanomorphanthridine (24a) and (2*S**,3*R**,4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-*syn*-3-Acetoxy-2-(benzyloxy)-8,9-(methylenedioxy)-5,11-methanomorphanthridine (24b). 24a.** A mixture of alcohol **23a** (15.5 mg, 0.04 mmol), $Ac_2O$ (17.7 mg, 0.17 mmol), and DMAP (7.8 mg, 0.06 mmol) in pyridine (0.5 mL) was stirred at rt for 1.5 h. After $H_2O$ was added, the mixture was extracted with $CHCl_3$. The organic extract was dried ($K_2CO_3$) and evaporated. Purification of the crude residue by silica gel preparative TLC (15:1 $CHCl_3$–MeOH) gave **24a** (16.1 mg, 93.5%): mp 185–187 °C; $^1H$ NMR (500 MHz) $\delta$ 7.27–7.33 (5 H, m, arom H×5), 6.51, 6.45 (each 1 H, s, arom H×2), 5.88, 5.87 (each 1 H, d, $J$ = 1.5 Hz, $OCH_2O$), 5.26 (1 H, dd, $J$ = 3.5, 7.5 Hz, H-2), 4.66, 4.50 (each 1 H, d, $J$ = 11.5 Hz, $CH_2Ph$), 4.24, 3.76 (each 1 H, d, $J$ = 16.5 Hz, H-6×2), 3.70 (1 H, dt, $J$ = 4, 9.5 Hz, H-3), 3.31 (1 H, dd, $J$ = 7, 13 Hz, H-4a), 3.09 (1 H, dd, $J$ = 2, 11.5 Hz, H-12), 2.93 (1 H, d, $J$ = 11.5 Hz, H-12), 2.58 (1 H, d, $J$ = 2 Hz, H-11), 2.55 (1 H, dt, $J$ = 7.5, 11.5 Hz, H-11a), 2.19 (1 H, ddd, $J$ = 7, 9, 14 Hz, H-4), 2.11 (1 H, ddd, $J$ = 3, 7, 15.5 Hz, H-1), 1.91 (1 H, dt, $J$ = 5, 14 Hz, H-4), 1.50 (1 H, ddd, $J$ = 4, 11.5, 15.5 Hz, H-1); IR 1740, 1500, 1480 $cm^{-1}$; MS $m/z$ 421 ($M^+$); high-resolution mass $m/z$ calcd for $C_{25}H_{27}NO_5$ ($M^+$) 421.1888, found 421.1888.

**24b.** A mixture of alcohol **23b** (15.0 mg, 0.04 mmol), $Ac_2O$ (18.6 mg, 0.18 mmol), and DMAP (8.4 mg, 0.07 mmol) in pyridine (0.3 mL) was stirred at rt for 17 h. Workup as described above afforded **24b** (13.2 mg, 79.2%): oil; $^1H$ NMR (500 MHz) $\delta$ 7.28–7.33 (5 H, m, arom H×5), 6.51, 6.45 (each 1 H, s, arom H×2), 5.88 (2 H, s, $OCH_2O$), 5.01 (1 H, dt, $J$ = 4, 9.5 Hz, H-3), 4.54, 4.51 (each 1 H, d, $J$ = 12 Hz, $CH_2Ph$), 4.23, 3.75 (each 1 H, d, $J$ = 16.5 Hz, H-6×2), 3.82 (1 H, dd, $J$ = 4, 7 Hz, H-2), 3.30 (1 H, dd, $J$ = 7, 12.5 Hz, H-4a), 3.14 (1 H, dd, $J$ = 3, 11.5 Hz, H-12), 2.93 (1 H, d, $J$ = 11.5 Hz, H-12), 2.60 (1 H, dt, $J$ = 7, 11.5 Hz, H-11a), 2.58 (1 H, d, $J$ = 3 Hz, H-11), 2.29 (1 H, ddd, $J$ = 7, 9.5, 14 Hz, H-4), 2.15 (1 H, ddd, $J$ = 4, 11.5, 14.5 Hz, H-1), 1.84 (1 H, dt, $J$ = 4, 14 Hz, H-4), 1.44 (1 H, ddd, $J$ = 3.5, 12, 14.5 Hz, H-1); IR 1730, 1500, 1480 $cm^{-1}$; MS $m/z$ 421 ($M^+$); high-resolution mass $m/z$ calcd for $C_{25}H_{27}NO_5$ ($M^+$) 421.1888, found 421.1885.

**(3*R**,4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-syn-3-(Benzyloxy)-2-oxo-8,9-(methylenedioxy)-5,11-methanomorphanthridine (25).** To an ice-cold, stirred solution of alcohol **23a** (380 mg, 1.0 mmol) in acetone (10 mL) was added 2 M Jones reagent (1.5 mL, 3 mmol), and stirring was continued at the same temperature for 10 min. Then *i*-PrOH (2 mL) and $H_2O$ were added to the mixture. After the mixture was made alkaline with solid $K_2CO_3$, the precipitate was filtered through a short pad of Celite 545. The filtrate was extracted with $CHCl_3$, and the extract was washed with $H_2O$ and brine, successively. Removal of the solvent in vacuo followed by silica gel column chromatography (30:1 $CHCl_3$–MeOH) gave **25** (222.7 mg, 58.9%): oil; $^1H$ NMR $\delta$ 7.28 (5 H, s, arom H×5), 6.46, 6.42 (each 1 H, s, arom H×2), 5.86 (2 H, s, $OCH_2O$), 4.71, 4.51 (each 1 H, d, $J$ = 12 Hz, $CH_2Ph$), 4.29, 3.76 (each 1 H, d, $J$ = 16.6 Hz, H-6×2), 3.67 (1 H, t, $J$ = 3.2 Hz, H-3), 3.52 (1 H, dt, $J$ = 6.4, 11.4 Hz, H-4a), 3.08 (1 H, dd, $J$ = 2, 7.1 Hz, H-12), 2.12–2.84 (5 H, m, H-1×2, H-4, H-11a, H-12), 1.83 (1 H, ddd, $J$ = 2.9, 11.4, 14.3 Hz, H-4); IR 1725, 1500, 1480 $cm^{-1}$; MS $m/z$ 377 ($M^+$); high-resolution mass $m/z$ calcd for $C_{23}H_{23}NO_4$ ($M^+$) 377.1625, found 377.1620.

**(3*R**,4a*R**,11*R**)-5,11a-*cis*-11,11a-*syn*-3-(Benzyloxy)-2-oxo-8,9-(methylenedioxy)-$\Delta^{1(11a)}$-5,11-methanomorphanthridine (26).** A mixture of ketone **25** (50.1 mg, 0.133 mmol), DDQ (90.8 mg, 0.40 mmol), and $Na_2HPO_4$ (57.7 mg, 0.406 mmol) in dioxane (1.5 mL) was refluxed for 1 h. $H_2O$ was added to the reaction mixture, and the mixture was extracted with $CHCl_3$. The organic extract was washed with saturated $NaHCO_3$ and brine, successively, and dried ($K_2CO_3$). Removal of the solvent in vacuo followed by silica gel preparative TLC (20:1 $CHCl_3$–MeOH) produced **26** (13.1 mg, 26.3%) and **25** (7.7 mg, 15.4%). **26**: oil; $^1H$ NMR $\delta$ 7.28 (5 H, s, arom H×5), 6.54, 6.46 (each 1 H, s, arom H×2), 5.90, 5.87 (each 1 H, d, $J$ = 1.4 Hz, $OCH_2O$), 5.76–5.92 (1 H, m, H-1), 4.64, 4.44 (each 1 H, d, $J$ = 11.4 Hz, $CH_2Ph$), 4.36, 3.85 (each 1 H, d, $J$ = 16.9 Hz, H-6×2), 3.60–4.06 (2 H, m, H-3, H-4a), 3.40 (1 H, s, H-11), 3.15 (2 H, s, H-12×2), 2.58 (1 H, ddd, $J$ = 2.6, 5.1, 12.9 Hz, H-4), 1.92 (1 H, ddd, $J$ = 2.6, 11.7, 12.9 Hz, H-4); IR 1670, 1510, 1485 $cm^{-1}$; MS $m/z$ 375 ($M^+$); high-resolution mass $m/z$ calcd for $C_{23}H_{21}NO_4$ ($M^+$) 375.1469, found 375.1464.

**(3*R**,4a*R**,11*R**)-5,11a-*cis*-11,11a-*syn*-3-(Benzyloxy)-2,2-dimethoxy-$\Delta^{1(11a)}$-8,9-(methylenedioxy)-5,11-methanomorphanthridine (27).** A mixture of enone **26** (34.7 mg, 0.093 mmol), trimethyl orthoformate (70.0 mg, 0.66 mmol), and *p*-TsOH·$H_2O$ (27.6 mg, 0.145 mmol) in MeOH (1.5 mL) was stirred at rt for 2 h. After addition of $H_2O$ to the mixture, the aqueous layer was made alkaline with saturated $NaHCO_3$. The mixture was extracted with $CHCl_3$, and usual workup of the extract gave an oily residue, which was purified by silica gel preparative TLC (20:1 $CHCl_3$–MeOH) to afford **27** (38.6 mg, 99.1%): oil; $^1H$ NMR $\delta$ 7.28 (5 H, s, arom H×5), 6.48, 6.40 (each 1 H, s, arom H×2), 5.85, 5.84 (each 1 H, d, $J$ = 1.3 Hz, $OCH_2O$), 5.60 (1 H, t, $J$ = 1.5 Hz, H-1), 4.57 (2 H, s, $CH_2Ph$), 4.28, 3.68 (each 1 H, d, $J$ = 16 Hz, H-6×2), 3.44–3.82 (2 H, m, H-3, H-4a), 3.22 (4 H, s, Me, H-11), 3.18 (3 H, s, Me), 3.04 (2 H, s, H-12), 2.42 (1 H, dt, $J$ = 4.4, 12 Hz, H-4), 1.90 (1 H, ddd, $J$ = 2, 11.4, 12 Hz, H-4); IR 1500, 1480 $cm^{-1}$; MS $m/z$ 421 ($M^+$); high-resolution mass $m/z$ calcd for $C_{25}H_{27}NO_5$ ($M^+$) 421.1887, found 421.1889.

**(±)-*O*-Benzylcoccinine (28).** A mixture of acetal **27** (15.4 mg, 0.037 mmol) and DIBAH (0.25 mL, 1 M in toluene) in toluene (1 mL) under Ar was stirred at rt for 1 h. A workup similar to that noted for **22** followed by silica gel preparative TLC (15:1 $CHCl_3$–MeOH) produced **28** (11.3 mg, 79.0%): mp 117 °C; $^1H$ NMR $\delta$ 7.16–7.40 (5 H, m, arom H×5), 6.49, 6.41 (each 1 H, s, arom H×2), 5.85 (2 H, s, $OCH_2O$), 5.44–5.60 (1 H, m, H-1), 4.63 (2 H, s, $CH_2Ph$), 4.28, 3.72 (each 1 H, d, $J$ = 16.8 Hz, H-6×2), 3.79–4.04 (2 H, m, H-2, H-3), 3.32 (3 H, s, Me), 3.21 (1 H, s, H-11), 3.02 (2 H, s, H-12), 2.45 (1 H, dt, $J$ = 4.4, 12 Hz, H-4), 1.50 (1 H, ddd, $J$ = 2.4, 11.4, 12 Hz, H-4); IR 1500, 1480 $cm^{-1}$; MS $m/z$ 391 ($M^+$); high-resolution mass $m/z$ calcd for $C_{24}H_{25}NO_5$ ($M^+$) 391.1782, found 391.1801.

**(±)-Coccinine (2).** A solution of benzyl ether **28** (6.3 mg, 0.016 mmol) and TMS-I (23 $\mu$L, 0.16 mmol) in $CHCl_3$ (0.25 mL) was stirred at rt for 5 h. After $H_2O$ and 10% $Na_2S_2O_3$ were added to the mixture, the aqueous layer was washed with $CHCl_3$. Then the aqueous layer was made alkaline with 3 M NaOH and extracted with $CHCl_3$. The extract was washed with brine and dried ($K_2CO_3$), and the solvent was removed in vacuo to give a residue, which was purified by silica gel column chromatography (30:1 and 10:1 $CHCl_3$–MeOH) to afford **2** (4.2 mg, 86.7%): mp 71–73 °C; $^1H$ NMR (500 MHz) $\delta$ 6.53, 6.45 (each 1 H, s, arom H×2), 5.89, 5.86 (each 1 H, d, $J$ = 2 Hz, $OCH_2O$), 5.52–5.53 (1 H, brs, $W_{1/2}$ = 7.9 Hz, H-1), 4.30, 3.84 (each 1 H, d, $J$ = 17 Hz, H-6×2), 4.29–4.38 (1 H, m, H-3), 3.85 (1 H, dd, $J$ = 4, 6 Hz, H-2), 3.67–3.72 (1 H, m, H-4a), 3.44 (3 H, s, OMe), 3.22 (1 H, d, $J$ = 2 Hz, H-11), 3.05 (1 H, d, $J$ = 11.5 Hz, H-12), 3.02 (1 H, dd, $J$ = 2, 11.5 Hz, H-12), 2.53 (1 H, dt, $J$ = 4.5, 13 Hz, H-4), 1.53 (1 H, ddd, $J$ = 2, 11.5, 13 Hz, H-4); IR 2925, 1500, 1480 $cm^{-1}$; MS $m/z$ 301 ($M^+$); high-resolution mass $m/z$ calcd for $C_{17}H_{19}NO_4$ ($M^+$) 301.1313, found 301.1316.

**(2*S**,3*R**,4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-*syn*-3-(Benzyloxy)-2-(mesyloxy)-8,9-(methylenedioxy)-5,11-methanomorphanthridine (29).** To an ice-cold, stirred solution of alcohol **23a** (207 mg, 0.546 mmol) and $Et_3N$ (190.6 mg, 1.88 mmol) in $CH_2Cl_2$ (5 mL) was added mesyl chloride (160 mg, 1.4 mmol) in $CH_2Cl_2$ (0.5 mL), and stirring was continued for 10 min. Usual workup of the mixture afforded **29** (249.3 mg, 100%): mp 182 °C (AcOEt–hexane); $^1H$ NMR $\delta$ 7.30 (5 H, s, arom H×5), 6.48, 6.42 (each 1 H, s, H-7, H-10), 5.86 (2 H, s, $OCH_2O$), 5.09 (1 H, dd, $J$ = 2.9, 5.7 Hz, H-2), 4.60 (2 H, s, $CH_2Ph$), 4.21, 3.73 (each 1 H, d, $J$ = 16.6 Hz, H-6×2), 3.59 (1 H, ddd, $J$ = 2.3, 5.7, 12 Hz, H-3), 3.18–3.40 (1 H, m, H-4a), 2.99 (1 H, dd, $J$ = 2, 5.7 Hz, H-12), 2.96 (3 H, s, $SO_2Me$), 2.46–2.72 (2 H, m, H-11, H-12), 1.76–2.40 (4 H, m, H-1, H-4×2, H-11a), 1.52 (1 H, ddd, $J$ = 3.4, 10.4, 14.9 Hz, H-4); IR 1500, 1480 $cm^{-1}$; MS $m/z$ 457 ($M^+$). Anal. Calcd for $C_{24}H_{27}NO_6S$: C, 63.00; H, 5.95; N, 3.06; S, 7.01. Found: C, 62.93; H, 5.90; N, 3.00; S, 7.10.

**(3*R**,4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-*syn*-3-(Benzyloxy)-$\Delta^{1(2)}$-8,9-(methylenedioxy)-5,11-methanomorphanthridine (30a) and (4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-*syn*-3-(Benzyloxy)-$\Delta^{2(3)}$-8,9-(methylenedioxy)-5,11-methanomorphanthridine (30b).** A solution of mesylate **29** (748 mg, 1.64 mmol) and *t*-BuOK (380.1 mg, 3.39 mmol) in DMSO (17 mL) was stirred at rt for 2 h. After $H_2O$ was added, the product was taken

up in ether. Workup of the ether extract as usual gave an oily residue, which was purified by silica gel column chromatography (50:1 $CHCl_3$–MeOH) to afford **30a** (415.9 mg, 70.4%) and **30b** (30.6 mg, 5.2%). **30a**: oil; $^1H$ NMR $\delta$ 7.20–7.40 (5 H, m, arom H×5) 6.54, 6.44 (each 1 H, s, arom H×2), 6.04 (1 H, ddd, $J$ = 1.7, 4.3, 10.6 Hz, olefinic H), 5.86 (2 H, s, $OCH_2O$), 5.68 (1 H, ddd, $J$ = 2.9, 4, 10.6 Hz, olefinic H), 4.61 (2 H, s, $CH_2Ph$), 4.58 (1 H, dd, $J$ = 2, 8 Hz, H-3), 4.26, 3.79 (each 1 H, d, $J$ = 17.1 Hz, H-6×2), 4.00–4.20 (1 H, m, H-3), 3.35 (1 H, dt, $J$ = 4, 10 Hz, H-4a), 1.96–3.02 (5 H, m, H-4, H-11, H-11a, H-12×2), 1.57 (1 H, ddd, $J$ = 5.2, 10, 12.9 Hz, H-4); IR 1500, 1480 $cm^{-1}$; MS $m/z$ 361 ($M^+$); high-resolution mass $m/z$ calcd for $C_{23}H_{23}NO_3$ ($M^+$) 361.1676, found 361.1673. **30b**: oil; $^1H$ NMR $\delta$ 7.30 (5 H, s, arom H×5), 6.47, 6.42 (each 1 H, s, H-7, H-10), 5.84 (2 H, s, $OCH_2O$), 4.62 (2 H, s, $CH_2Ph$), 4.56–4.80 (1 H, m, H-2), 4.29, 3.72 (each 1 H, d, $J$ = 17.1 Hz, H-6×2), 3.04–3.48 (3 H, m), 2.80–3.02 (1 H, m), 2.06–2.70 (5 H, m); MS $m/z$ 361 ($M^+$); high-resolution mass $m/z$ calcd for $C_{23}H_{23}NO_3$ ($M^+$) 361.1676, found 361.1676.

**(2*R**,3*R**,4a*R**,11*S**)-5,11a-*cis*-11,11a-*syn*-3-(Benzyloxy)-2-chloro-$\Delta^{1(11a)}$-8,9-(methylenedioxy)-5,11-methanomorphanthridine (31) and (3*R**,4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-*syn*-3-(Benzyloxy)-1-chloro-$\Delta^{1(2)}$-8,9-(methylenedioxy)-5,11-methanomorphanthridine (32).** A solution of olefin **30a** (16.3 mg, 0.045 mmol) and PhSeCl (18.2 mg, 0.095 mmol) in MeOH (2 mL) was refluxed for 1 h. After cooling, the mixture was treated with $NaIO_4$ (24.0 mg, 0.112 mmol) in $H_2O$ (0.5 mL) at rt for 10 min. The mixture was made alkaline with 3 M NaOH and extracted with $CHCl_3$. The organic extract was washed with brine and dried ($K_2CO_3$). Evaporation of the solvent in vacuo gave an oily residue, which was purified by silica gel preparative TLC (30:1 $CHCl_3$–MeOH) to afford **31** (4.1 mg, 23.0%) and **32** (4.9 mg, 27.8%). **31**: oil; $^1H$ NMR (500 MHz) $\delta$ 7.26–7.35 (5 H, m, arom H×5), 6.53 (1 H, s, H-10), 6.46 (1 H, s, H-7), 5.88, 5.86 (each 1 H, d, $J$ = 1.5 Hz, $OCH_2O$), 5.56–5.58 (1 H, m, H-1), 4.61, 4.56 (each 1 H, d, $J$ = 12 Hz, $CH_2Ph$), 4.42–4.52 (1 H, m, H-2), 4.32, 3.79 (each 1 H, d, $J$ = 16.5 Hz, H-6×2), 4.02–4.06 (1 H, m, H-3), 3.46–3.51 (1 H, m, H-4a), 3.28 (1 H, d, $J$ = 2 Hz, H-11), 3.90 (1 H, d, $J$ = 11 Hz, H-12), 3.34 (1 H, dd, $J$ = 2, 11 Hz, H-12), 2.27 (1 H, ddd, $J$ = 3.5, 5, 12.5 Hz, H-4), 1.69 (1 H, dt, $J$ = 2, 12.5 Hz, H-4); IR 1500, 1480 $cm^{-1}$; MS $m/z$ 395 ($M^+$), 397 ($M^+$ + 2); high-resolution mass $m/z$ calcd for $C_{23}H_{22}NO_3Cl$ ($M^+$) 395.1287, found 395.1303. **32**: oil; $^1H$ NMR (500 MHz) $\delta$ 7.27–7.35 (5 H, m, arom H×5), 6.62 (1 H, s, H-10), 6.46 (1 H, s, H-7), 6.20 (1 H, s, H-2), 5.90 (2 H, s, $OCH_2O$), 4.61 (2 H, s, $CH_2Ph$), 4.22, 3.78 (each 1 H, d, $J$ = 16 Hz, H-6×2), 4.12 (1 H, ddd, $J$ = 2.5, 5, 10.3 Hz, H-3), 3.38–3.40 (1 H, m, H-4a), 3.18 (1 H, d, $J$ = 2 Hz, H-11), 3.01 (1 H, d, $J$ = 6.5 Hz, H-11a), 2.88 (1 H, d, $J$ = 11.5 Hz, H-12), 2.75 (1 H, dd, $J$ = 2, 11.5 Hz, H-12), 2.48 (1 H, dt, $J$ = 4, 12.5 Hz, H-4), 1.53 (1 H, ddd, $J$ = 5, 10.3, 12.5 Hz, H-4); IR 1500, 1480, 1450 $cm^{-1}$; MS $m/z$ 395 ($M^+$), 397 ($M^+$ + 2); high-resolution mass $m/z$ calcd for $C_{23}H_{22}NO_3Cl$ ($M^+$) 395.1287 found 395.1283.

**(3*R**,4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-*syn*-3-Hydroxy-$\Delta^{1(2)}$-8,9-(methylenedioxy)-5,11-methanomorphanthridine (33) and (4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-*syn*-3-(methylthio)-$\Delta^{1(2)}$-8,9-(methylenedioxy)-5,11-methanomorphanthridine (34).** A solution of olefin **30a** (45.5 mg, 0.126 mmol), $BF_3{\cdot}EtO_2$ (0.3 mL), and $Me_2S$ (0.2 mL) in $CH_2Cl_2$ (0.4 mL) was stirred at rt for 5 h. After 3 M NaOH was added, the mixture was extracted with $CHCl_3$. The solvent was dried ($K_2CO_3$) and removed in vacuo. Purification of the residue by silica gel preparative TLC (10:1 $CHCl_3$–MeOH) gave **33** (14.9 mg, 43.6%), **34** (5.0 mg, 13.2%) and **30a** (7.3 mg, 16.0%). **33**: mp 226–227 °C (AcOEt–hexane); $^1H$ NMR $\delta$ 6.54, 6.44 (each 1 H, s, arom H×2), 5.96 (1 H, ddd, $J$ = 1.4, 2.3, 10.6 Hz, olefinic H), 5.88 (2 H, s, $OCH_2O$), 5.65 (1 H, ddd, $J$ = 2.3, 4.3, 10.6 Hz, olefinic H), 4.22–4.48 (1 H, m, H-3), 4.24, 3.78 (each 1 H, d, $J$ = 16 Hz, H-6×2), 3.32 (1 H, dt, $J$ = 4, 8 Hz, H-4a), 2.68–2.98 (4 H, m, H-11, H-11a, H-12×2), 2.32–2.58 (1 H, m, H-4), 1.46 (1 H, ddd, $J$ = 4, 10, 13.1 Hz, H-4); IR 3600, 1500, 1480 $cm^{-1}$; MS $m/z$ 271 ($M^+$); high-resolution mass $m/z$ calcd for $C_{16}H_{17}NO_3$ ($M^+$) 271.1208, found 271.1209. **34**: oil; $^1H$ NMR $\delta$ 6.50, 6.44 (each 1 H, s, arom H×2), 5.86 (2 H, s, $OCH_2O$), 5.66–5.90 (1 H, m, olefinic H), 5.42 (1 H, d, $J$ = 3.1 Hz), 4.32, 3.80 (each 1 H, d, $J$ = 17 Hz, H-6×2), 3.34–3.52 (1 H, m, H-4a), 3.08 (1 H, dd, $J$ = 2.3, 11.4 Hz, H-12), 2.88 (1 H, d, $J$ = 11.4 Hz, H-12), 2.67 (1 H, d, $J$ = 2.3 Hz, H-11), 2.52–2.72 (3 H, m, H-3, H-4, H-11a), 2.26 (3 H, s, SMe), 1.80–2.05 (1 H, m, H-4); IR 2925, 1500, 1480 $cm^{-1}$; MS $m/z$ 301 ($M^+$); high-resolution mass $m/z$ calcd for $C_{17}H_{19}NO_2S$ ($M^+$) 301.1135, found 301.1139.

**(2*S**,3*R**,4a*R**,11*S**)-5,11a-*cis*-11,11a-*syn*-2,3-Epoxy-$\Delta^{1(11a)}$-8,9-(methylenedioxy)-5,11-methanomorphanthridine (35) and (3*R**,4a*R**,11*S**,11a*R**)-5,11a-*cis*-11,11a-*syn*-1- or -2-Chloro-3-hydroxy-$\Delta^{1(2)}$-8,9-(methylenedioxy)-5,11-methanomorphanthridine (36).** A mixture of allylic alcohol **33** (12.2 mg, 0.045 mmol) and PhSeCl (18.4 mg, 0.096 mmol) in MeOH (1 mL) was stirred for rt for 3 days. Then $NaIO_4$ (31.6 mg, 0.147 mmol) in $H_2O$ (0.3 mL) was added to the mixture. After 10 min, 3 M NaOH was added to the mixture, which was then extracted with $CHCl_3$. The extract was washed with brine and dried ($K_2CO_3$), and the solvent was removed in vacuo to give a crude residue, which was purified by silica gel preparative TLC (10:1 $CHCl_3$–MeOH) to afford **35** (4.9 mg, 40.5%) and **36** (2.9 mg, 21.1%). **35**: mp 144 °C (hexane); $^1H$ NMR $\delta$ 6.50, 6.44 (each 1 H, s, arom H×2), 5.86, 5.84 (each 1 H, d, $J$ = 1.2 Hz, $OCH_2O$), 5.51–5.92 (1 H, m, H-1), 4.32, 3.73 (each 1 H, d, $J$ = 16 Hz, H-6×2), 3.14–3.52 (4 H, m, H-2, H-3, H-11, H-11a), 2.88–3.02 (1 H, m, H-12), 2.69 (1 H, ddd, $J$ = 2.4, 8, 14 Hz, H-4), 1.30 (1 H, dd, $J$ = 12, 14 Hz, H-4); IR 1500, 1480 $cm^{-1}$; MS $m/z$ 269 ($M^+$); high-resolution mass $m/z$ calcd for $C_{16}H_{15}NO_3$ ($M^+$), 269.1050, found 269.1050. **36**: oil; $^1H$ NMR $\delta$ 6.60, 6.44 (each 1 H, s, arom H×2), 6.08 (1 H, brs, $W_{1/2}$ = 3.7 Hz, H-2), 5.88 (2 H, s, $OCH_2O$), 4.22–4.48 (1 H, m, H-3), 4.24, 3.76 (each 1 H, d, $J$ = 16.6 Hz, H-6×2), 3.26–3.48 (1 H, m, H-4a), 3.18 (1 H, brs, $W_{1/2}$ = 3.7 Hz, H-11a), 2.98 (1 H, d, $J$ = 6 Hz, H-11), 2.76–2.90 (2 H, m, H-12×2), 2.28–2.56 (1 H, m, H-4), 1.36–1.60 (1 H, m, H-4); MS $m/z$ 305 ($M^+$), 307 ($M^+$ + 2); high-resolution mass $m/z$ calcd for $C_{16}H_{16}NO_3Cl$ ($M^+$) 305.0817, found 305.0810.

**Reaction of 30a with Phenylselenenyl Chloride under Ultrasonication.** A mixture of benzyl ether **30a** (1.6861 g, 4.67 mmol) and PhSeCl (2.2360 g, 11.7 mmol) in MeOH (50 mL) was sonicated at 15–20 °C for 2 h. Then a solution of $NaIO_4$ (3.0012 g, 14.0 mmol) in $H_2O$ (20 mL) was added to the mixture, and stirring was continued for 10 min. A workup similar to that described above afforded a residue, which was purified by silica gel column chromatography (50:1 $CHCl_3$–MeOH) to give **31** (1.5202 g, 82.3%). Its spectra were identical with those of authentic sample obtained above.

**(±)-Montanine (1).** An ice-cold solution of allylic epoxide **35** (174.0 mg, 0.647 mmol) and $BF_3{\cdot}Et_2O$ (0.35 mL, 2.84 mmol) in MeOH (5 mL) was stirred for 15 min. After the mixture was made alkaline with 3 M NaOH, the mixture was extracted with $CHCl_3$. Usual workup of the extract gave a crude residue, which was purified by silica gel preparative TLC (10:1 $CHCl_3$–MeOH) to afford (±)-**1** (183.5 mg, 94.2%): mp 201–202 °C (acetone); $^1H$ NMR (500 MHz) $\delta$ 6.55, 6.46 (each 1 H, s, H-7, H-10), 5.89, 5.87 (each 1 H, d, $J$ = 1.5 Hz, $OCH_2O$), 5.57 (1 H, brs, $W_{1/2}$ = 5.7 Hz, H-1), 4.35, 3.82 (each 1 H, d, $J$ = 17 Hz, H-6×2), 4.09 (1 H, dd, $J$ = 2.5, 7.2 Hz, H-3), 3.48 (1 H, dd, $J$ = 2.5, 4 Hz, H-2), 3.44 (3 H, s, OMe), 3.39–3.45 (1 H, m, H-4a), 3.29 (1 H, d, $J$ = 2.5 Hz, H-11), 3.09 (1 H, dd, $J$ = 2.5, 12 Hz, H-12), 3.04 (1 H, d, $J$ = 12 Hz, H-12), 2.17 (1 H, ddd, $J$ = 3, 5.5, 13 Hz, H-4), 1.58 (1 H, ddd, $J$ = 4, 12, 13 Hz, H-4); IR 2925, 1500, 1480 $cm^{-1}$; MS $m/z$ 301 ($M^+$). Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.65; H, 6.25; N, 4.67.

**(±)-*O*-Acetylmontanine (3).** A mixture of **1** (9.6 mg, 0.032 mmol), $Ac_2O$ (0.05 mL), and DMAP (0.3 mg, 0.0024 mmol) in pyridine (0.5 mL) was stirred at rt for 15 h. Removal of the solvent in vacuo followed by purification by silica gel preparative TLC (10:1 $CHCl_3$–MeOH) gave **3** (9.6 mg, 87.8%): mp 173–174 °C; $^1H$ NMR $\delta$ 6.56, 5.48 (each 1 H, s, H-7, H-10), 5.89, 5.87 (each 1 H, d, $J$ = 1.2 Hz, $OCH_2O$), 5.44–5.58 (1 H, m, H-1), 5.12–5.24 (1 H, m, H-3), 4.90 (1 H, brs, $W_{1/2}$ = 10 Hz, H-2), 4.39, 3.84 (each 1 H, d, $J$ = 16 Hz, H-6×2), 3.47 (3 H, s, OMe), 3.24–3.50 (2 H, m, H-4a, H-11), 3.06 (2 H, brs, $W_{1/2}$ = 2.9 Hz, H-12), 2.22 (1 H, ddd, $J$ = 3.4, 5.7, 12.3 Hz, H-4), 2.02 (3 H, s, OAc), 1.58 (1 H, ddd, $J$ = 3.4, 11.7, 12.3 Hz, H-4); IR 1725, 1500, 1480 $cm^{-1}$; MS $m/z$ 343 ($M^+$); high-resolution mass $m/z$ calcd for $C_{19}H_{21}NO_5$ ($M^+$) 343.1419, found 343.1422.

**(±)-Pancracine (4).** A solution of allylic epoxide **35** (26.9 mg, 0.1 mmol) and 3 N $H_2SO_4$ (1 mL) in THF (1 mL) was refluxed for 5 h. After the mixture was made alkaline with 3 M NaOH, the mixture was extracted with $CHCl_3$ containing a small amount of MeOH. The organic extract was washed with brine and dried

($K_2CO_3$). Evaporation of the solvent in vacuo gave colorless crystals, which were washed with $CHCl_3$ to give **4** (22.5 mg, 78.4%): mp > 280 °C; $^1H$ NMR (DMSO-$d_6$) $\delta$ 6.64, 6.55 (each 1 H, s, arom H×2), 5.88, 5.84 (each 1 H, d, $J$ = 1.2 Hz, $OCH_2O$), 5.34 (1 H, brs, $W_{1/2}$ = 5.7 Hz, H-1), 4.52–4.82 (2 H, m, H-2, H-3), 4.15, 3.62 (each 1 H, d, $J$ = 16 Hz, H-6×2); IR (KBr) 3200–3650, 1500, 1480 $cm^{-1}$; MS $m/z$ 287 ($M^+$); high-resolution mass $m/z$ calcd for $C_{16}H_{17}NO_4$ ($M^+$) 287.1156, found 287.1156.

**(±)-Diacetylpancracine (37).** A mixture of (±)-pancracine (**4**) (10.0 mg, 0.035 mmol), $Ac_2O$ (17.3 mg, 0.17 mmol), and DMAP (1.3 mg, 0.011 mmol) in pyridine (0.3 mL) was stirred at rt for 3.5 h. After addition of $H_2O$, the mixture was extracted with $CHCl_3$. The solvent was washed with brine and dried ($K_2CO_3$), and the solvent was evaporated in vacuo to give a crude residue, which was purified by silica gel preparative TLC (10:1 $CHCl_3$–MeOH) to produce **37** (10.8 mg, 83.5%): mp 152 °C; $^1H$ NMR $\delta$ 6.52, 6.47 (each 1 H, s, arom H×2), 5.88, 5.87 (each 1 H, d, $J$ = 1.2 Hz, $OCH_2O$), 5.41–5.50 (1 H, m, H-1), 4.96–5.18 (2 H, m, H-2, H-3), 4.36, 3.80 (each 1 H, d, $J$ = 16 Hz, H-6×2), 3.16–3.44 (2 H, m, H-4a, H-11), 3.06 (2 H, brs, $W_{1/2}$ = 4 Hz, H-12), 2.22 (1 H, ddd, $J$ = 2.9, 5.1, 12.9 Hz, H-4), 2.07, 2.02 (each 3 H, s, OAc×2), 1.55 (1 H, ddd, $J$ = 2.9, 12, 12.9 Hz, H-4); IR 1735, 1510, 1485 $cm^{-1}$; MS $m/z$ 371 ($M^+$); high-resolution mass $m/z$ calcd for $C_{20}H_{21}NO_6$ ($M^+$) 371.1367, found 371.1365. The $^1H$ NMR and mass spectra agreed with those reported in the literature.[27]

**(4a*R**,11*S**)-1,2,3,11a-Tetradehydro-8,9-(methylenedioxy)-5,11-methanomorphanthridine (38).** TMSCl (55 $\mu$L, 0.43 mmol) was added to a stirred suspension of NaI (126.2 mg, 0.84 mmol) in $CH_3CN$ (1.2 mL) at rt. After 2 min, allylic epoxide **35** (174.0 mg, 0.647 mmol) in $CH_3CN$ (0.3 mL) was added, and stirring was continued at rt for 0.5 h. Then $CHCl_3$ and 3 N NaOH were added to the mixture, and the aqueous layer was extracted with $CHCl_3$. The extract was washed with 10% $Na_2S_2O_3$ and brine, successively, and dried ($K_2CO_3$), and the solvent was evaporated in vacuo to give an oily residue, which was purified by silica gel preparative TLC (10:1 $CHCl_3$–MeOH) to produce **38** (23.4 mg, 55.3%) and **35** (19.0 mg, 42.2%). **38**: mp 59–60 °C; $^1H$ NMR $\delta$ 6.43, 6.52 (each 1 H, s, arom H×2), 5.84, 5.86 (each 1 H, d, $J$ = 1.2 Hz, $OCH_2O$), 5.52–5.96 (3 H, m, olefinic H), 3.76, 4.36 (each 1 H, d, $J$ = 17 Hz, H-6×2), 3.37–3.45 (1 H, m, H-4a), 3.37 (1 H, dd, $J$ = 2, 12 Hz, H-12), 3.31 (1 H, d, $J$ = 2 Hz, H-11), 3.10 (1 H, d, $J$ = 12 Hz, H-12), 2.08–2.61 (2 H, m, H-4); IR 1460 $cm^{-1}$; MS $m/z$ 253 ($M^+$); high-resolution mass $m/z$ calcd for $C_{16}H_{15}NO_2$ ($M^+$) 253.1101, found 253.1091.

**(±)-Diacetylbrunsvigine (39a) and (±)-2-Diacetylepipancracine (39b).** A mixture of diene **38** (10.0 mg, 0.04 mmol), $OsO_4$ (6 $\mu$L, 0.0012 mmol, 0.2 M in dioxane), and *N*-methylmorpholine *N*-oxide[11] (4.8 mg, 0.041 mmol) in dioxane (0.4 mL)–$H_2O$ (0.1 mL) was stirred at rt for 3 h. The reaction was quenched with 10% $Na_2S_2O_3$ and 1 N NaOH. The mixture was extracted with $CHCl_3$, and the extract was washed with brine. The solvent was dried ($K_2CO_3$) and evaporated in vacuo to give diastereomeric diols (11.3 mg, 99.6%). The diols (7.6 mg, 0.026 mmol) were treated with $Ac_2O$ (14.2 mg, 0.139 mmol) and DMAP (1.0 mg, 0.008 mmol) in pyridine (0.5 mL) at rt for 19 h. After the usual workup, the crude product was purified by silica gel preparative TLC (10:1 $CHCl_3$–MeOH) to produce **39a** (1.2 mg, 12.2%) and **39b** (8.5 mg, 86.5%). **39a**: mp 217–218 °C; $^1H$ NMR $\delta$ 6.51, 6.45 (each 1 H, s, H-7, H-10), 5.85, 5.87 (each 1 H, d, $J$ = 1.2 Hz, $OCH_2O$), 5.36–5.58 (2 H, m, H-1, H-2), 4.93 (1 H, dt, $J$ = 4, 12 Hz, H-3), 3.80, 4.29 (each 1 H, d, $J$ = 17.1 Hz, H-6×2), 3.18–3.42 (1 H, m, H-4a), 3.29 (1 H, s, H-11), 3.08 (2 H, s, H-12), 2.04–2.37 (1 H, m, H-4), 2.00, 2.08 (each 3 H, s, OAc×2), 1.52–1.92 (1 H, m, H-4); MS $m/z$ 371 ($M^+$); high-resolution mass $m/z$ calcd for $C_{20}H_{21}NO_6$ ($M^+$) 371.1368, found 371.1362. $^1H$ NMR spectral data for **39a** were identical with those reported in the literature.[5c] **39b**: mp 235–236.5 °C; $^1H$ NMR $\delta$ 6.42, 6.52 (each 1 H, s, H-7, arom H×2), 5.87 (2 H, s, $OCH_2O$), 5.32–5.56 (3 H, m, H-1, H-2, H-3), 3.80, 4.32 (each 1 H, d, $J$ = 16 Hz, H-6×2), 3.44–3.72 (1 H, m, H-4a), 3.26 (1 H, s, H-11), 3.04 (2 H, s, H-12), 2.22–2.30 (1 H, m, H-4), 1.99, 2.04 (each 3 H, s OAc×2), 1.56–1.90 (1 H, m, H-4); IR 1735 $cm^{-1}$; MS $m/z$ 371 ($M^+$); high-resolution mass $m/z$ calcd for $C_{20}H_{21}NO_6$ ($M^+$) 371.1368, found 371.1370.

**(±)-Brunsvigine (5).** A mixture of diacetate **39a** (1.3 mg, 0.0035 mmol) and NaOMe (2.0 mg, 0.037 mmol) in MeOH (0.3 mL) was stirred at rt for 20 min. After addition of brine, the product was taken up in $CHCl_3$. The $CHCl_3$ extract was washed with brine and dried ($K_2CO_3$), and the solvent was evaporated in vacuo to give **5** (0.9 mg, 89.5%): mp 255–257 °C; MS $m/z$ 287 ($M^+$); high-resolution mass $m/z$ calcd for $C_{16}H_{17}NO_4$ ($M^+$) 287.1156, found 287.1156.

**Oxidation of Allylic Chloride 31 to Enone (26).** A solution of allylic chloride **31** (13.5 mg, 0.034 mmol) and $(Bu_4)_2Cr_2O_7$ (62.4 mg, 0.17 mmol) in $CHCl_3$ (1 mL) was refluxed for 3 h. Then additional $(Bu_4)_2Cr_2O_7$ (62.4 mg, 0.17 mmol) was added to the mixture, and refluxing was continued for a further 25 h. After the addition of 3 N NaOH to the mixture, the aqueous layer was extracted with $CHCl_3$. The organic extract was washed with brine and dried ($K_2CO_3$), and the solvent was removed in vacuo to give an oily residue, which was purified by silica gel preparative TLC (20:1 $CHCl_3$–MeOH) to afford **26** (4.0 mg, 31.2%) and **31** (2.3 mg, 17.0%). Spectral data for **26** were identical with those for an authentic sample obtained from **25**.

**(±)-*O*-Benzylmontanine (40) and (±)-Montanine (1). 40.** A solution of allylic chloride **31** (31.2 mg, 0.079 mmol) and NaOMe (5.4 mg, 0.1 mmol) in MeOH (0.5 mL) was refluxed for 5 h. After $H_2O$ was added, the mixture was extracted with $CHCl_3$. The extract was washed with brine and dried ($K_2CO_3$), and the solvent was evaporated in vacuo to afford a residue, which was purified by silica gel preparative TLC (10:1 $CHCl_3$–MeOH) to give **40** (22.3 mg, 72.3%): oil; $^1H$ NMR $\delta$ 7.28 (5 H, m, arom H×5), 6.52, 6.43 (each 1 H, s, arom H×2), 5.87, 5.84 (each 1 H, d, $J$ = 1.6 Hz, $OCH_2O$), 5.52 (1 H, brs, $W_{1/2}$ = 5.7 Hz, m, H-1), 4.58 (2 H, s, $CH_2Ph$), 4.29, 3.77 (each 1 H, d, $J$ = 17.1 Hz, H-6×2), 3.50–3.90 (2 H, m, H-2, H-3), 3.33 (3 H, s, OMe), 3.12–3.50 (2 H, m, H-4a, H-11), 3.04 (2 H, s, H-12×2), 2.30 (1 H, ddd, $J$ = 3.6, 4.8, 12.8, 12 Hz, H-4), 1.41 (1 H, dt, $J$ = 3.6, 12.8 Hz, H-4); IR 1480 $cm^{-1}$; MS $m/z$ 391 ($M^+$); high-resolution mass $m/z$ calcd for $C_{24}H_{25}NO_4$ ($M^+$) 391.1781, found 391.1776.

1. A solution of benzyl ether **40** (10.4 mg, 0.027 mmol) and TMS-I (22 $\mu$L, 0.15 mmol) in $CHCl_3$ (0.25 mL) was stirred at rt for 1 h. A workup similar to that noted for **28** gave (±)-montanine (**1**) (3.0 mg, 37.5%), $^1H$ NMR and IR spectra of which were identical with those of the authentic sample obtained above.

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**Supplementary Material Available:** $^1H$ NMR spectra for compounds **24a**, **24b**, **25**, **27**, **28**, **30a**, **30b**, **33**, **34**, **35**, **36**, **38**, **39b** and **40** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.