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Pyrolysis and Photolysis of the N-Oxides of Protopines and Hexahydrobenzo[*c*]phenanthridines. Syntheses of the Secoberbines and Benzo[*c*]phenanthridines[1)]

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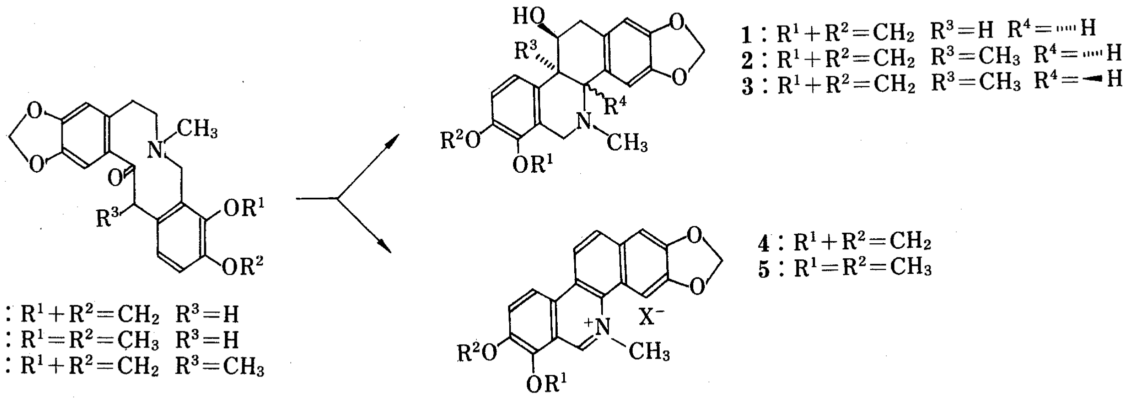
Pyrolysis and photolysis of the N-oxides of the protopines **9** and **16** produces the ring-enlarged compounds **10** and **17**, whose reduction with zinc in acetic acid leads to the secoberbines (±)-corydalisol (**11**) and (±)-hypecorine (**12**) from **9**, and the corresponding analogs (**18** and **19**) from **16**. Pyrolysis of (+)-chelidonine N-oxide (**24**) generates dihydrosanguinarine (**22**).

Keywords——pyrolysis; photolysis; N-oxide; protopine; sanguinarine; corydalisol; hypecorine

A number of protopine and benzo[*c*]phenanthridine type alkaloids have been isolated from intact plants and cell cultures of Papaveraceae plants.[2,3)] By feeding experiments, it has been demonstrated that the hexahydrobenzo[*c*]phenanthridines, such as (+)-chelidonine (**1**), (+)-corynoline (**2**) and (+)-14-epicorynoline (**3**), and the benzo[*c*]phenanthridines, such as sanguinarine (**4**) and chelerythrine (**5**), are formed from the corresponding protopines, such as protopine (**6**), allocryptopine (**7**), and corycavine (**8**) (Chart 1). The nature of the intermediates in this biosynthetic sequence has not yet been determined. Protopine N-oxide (**9**) was recently isolated from nature,[4)] and this alkaloid might be an important biosynthetic intermediate between the protopines and benzophenanthridine derivatives. There might be a biogenetic relationship between the hexahydrobenzo[*c*]phenanthridines (*e.g.* **1**) and the benzo[*c*]phenanthridines (*e.g.* **4**), though this has not previously been proposed. We become interested in the pyrolysis and photolysis of the N-oxides of protopines and hexahydrobenzo[*c*]phenanthridines (*e.g.* **9** and **24**) in the hope of obtaining some insight into the mechanisms of biosynthetic conversion of protopines to benzophenanthridine derivatives.



1 : $R^1+R^2=CH_2$ $R^3=H$ $R^4=$ ''''H
2 : $R^1+R^2=CH_2$ $R^3=CH_3$ $R^4=$ ''''H
3 : $R^1+R^2=CH_2$ $R^3=CH_3$ $R^4=$ ◀H

4 : $R^1+R^2=CH_2$
5 : $R^1=R^2=CH_3$

6 : $R^1+R^2=CH_2$ $R^3=H$
7 : $R^1=R^2=CH_3$ $R^3=H$
8 : $R^1+R^2=CH_2$ $R^3=CH_3$

Chart 1

Protopine N-oxide (**9**) was pyrolyzed by heating in a dry oven to 180 °C. The resultant mixture of three products was separated by careful preparative thin-layer chromatograph

(PTLC). From inspection of the spectral data (see Experimental), the main product [60% yield, m/z 369 (M$^+$)] was assumed to be the compound (**10**) formed by Meisenheimer rearrangement,[5] which has been already found to occur in the pyrolysis of tetrahydroisoquinoline N-oxide.[6] The structure of the ring-enlarged compound (**10**) was proved by the conversion of **10** into secoberbines. Reduction of **10** with zinc in acetic acid afforded two products together with 32% recovery of the starting material. The first product [20% yield, mp 147—148 °C, chemical ionization mass spectrum (CIMS) m/z 356 (M$^+$ + 1)] was identical with the naturally occurring (+)-corydalisol (**11**)[7] in terms of the infrared spectrum (IR) and proton nuclear magnetic resonance (^{1}H-NMR) spectrum. The other product [10% yield, mp 160—162 °C, m/z 353 (M$^+$)] from this reduction was considered to be (±)-hypecorine (**12**) from the spectral data (see Experimental). The second product [16% yield, mp 149—150 °C, m/z 369 (M$^+$)] of the pyrolysis of **9** was concluded to be the hydroxylamine (**13**) formed by a Cope elimination reaction[8] based on the spectral data (see Experimental). The ^{1}H-NMR spectrum of **13** showed typical styrene-type signals. The structure of **13** was further confirmed by its conversion to the O-acetyl derivative. Acetylation of **13** with acetic anhydride in pyridine furnished the amorphous acetate (**14**) [ν_{max} (CHCl$_3$) 1760 and 1685 cm^{-1}, m/z 411 (M$^+$)]. The ^{1}H-NMR spectrum of **14** showed a signal at δ 1.94 due to the acetyl group. The third product [4.6% yield, mp 159—162 °C, m/z 322 (M$^+$)] obtained from the pyrolysis of **9** showed a hydroxyl band in its IR spectrum and gave a C-methyl signal at δ 2.02 in the ^{1}H-NMR spectrum and a methyl signal at δ 12.43 in the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum. The signals of six aromatic protons were observed in the ^{1}H-NMR spectrum. The ^{13}C-NMR spectrum also showed the signals of six corresponding carbons. This product was assigned as the phenolic compound **15**, which was also formed by pyrolysis of **10**. Independently, Shamma *et al.*[1] recently synthesized compounds **10**, **11**, **12**, and **13** *via* a reaction sequence similar to ours.

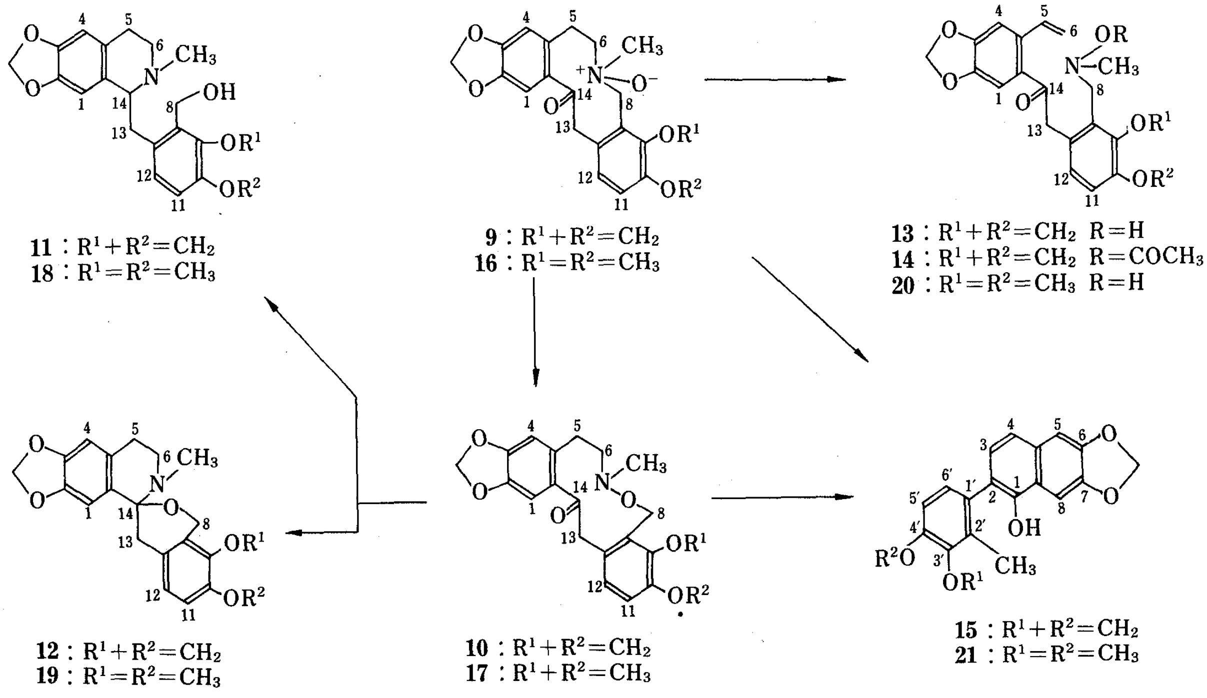


Chart 2

Pyrolysis of allocryptopine N-oxide (**16**) was carried out in order to examine the effect of the substituents at 9-C and 10-C in the N-oxide on attack at the benzylic position (8-C) by the amine oxide. Pyrolysis of allocryptopine N-oxide (**16**) gave three products, **17** (24% yield), **20**

(36% yield), and **21** (5.1% yield) which, were identified by analogy with those obtained from the pyrolysis of protopine N-oxide (**9**). The yield of the ring-enlarged product (**17**) was lower than with protopine N-oxide (**9**), and the more unsaturated hydroxylamine (**20**) was produced. The migration of the benzyl group from nitrogen to oxygen is thought to be somewhat affected by the substituents at 9-C and 10-C in the N-oxide. Pyrolysis of **17** gave **21** (11% yield) together with 60% recovery of **17**. As was the case with **10**, reduction of **17** with zinc in acetic acid gave two products, **18** and **19**, in 60 and 1.5% yields, respectively. The structure of **18** was identified by comparison of the product with an authentic sample.9) Assignment of structure **19** was made by comparison of the spectral data with those of **12**. Compounds **15** and **21** could be formed *via* **10** and **17** from **9** and **16**, respectively. A mechanism which explains the formation of the products (**10**, **13**, **17**, and **20**) of pyrolysis of the N-oxides **9** and **16** and the preparation of the secoberbines (**11**, **12**, **18**, and **19**) is presented in Chart 3.

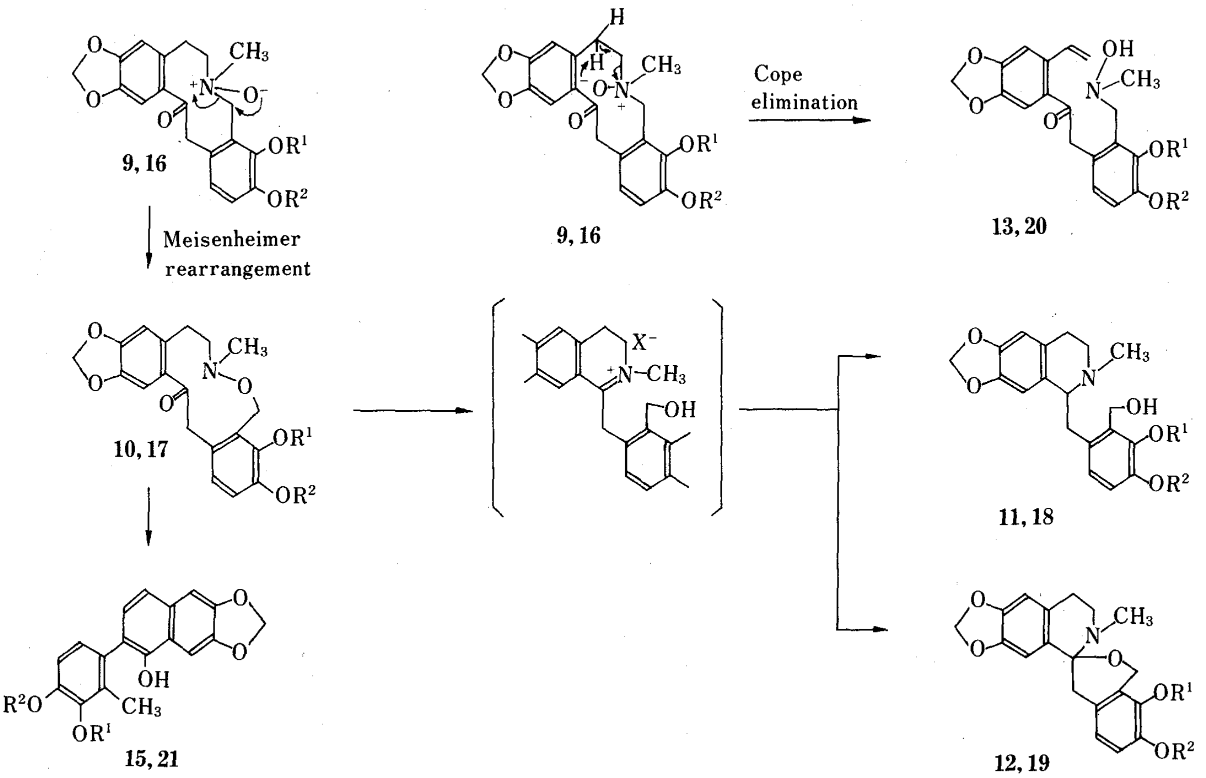
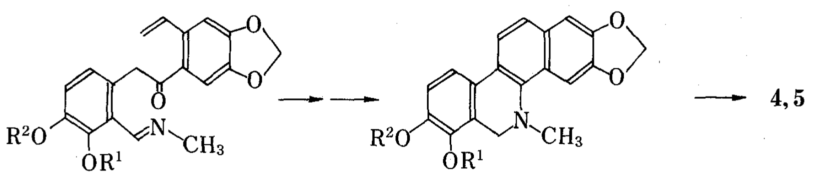


Chart 3

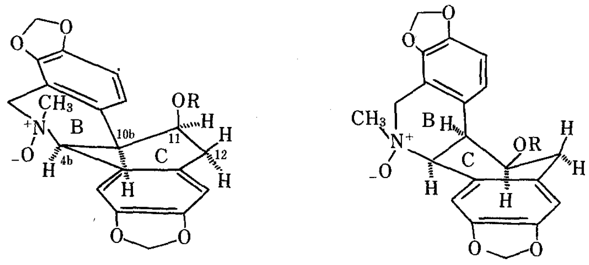
Irradiation of a methanolic solution of protopine N-oxide (**9**) furnished two products. The first product was identical with the compound (**10**) obtained from the pyrolysis of **9**. The second product was proved to be the benzo[*c*]phenanthridine, sanguinarine (**4**), since it was reduced by treatment with sodium borohydride in methanol to give dihydrosanguinarine (**22**), which was identical with an authentic sample in terms of the IR and ^{1}H-NMR spectra. Compound **10** and sanguinarine (**4**) were obtained in 24 and 1% yields, respectively, along with 37% recovery of the starting N-oxide. Photolysis of allocryptopine N-oxide (**16**) also afforded **17** and chelerythrine (**5**) in 15 and 2% yields, respectively, together with 33% recovery of the starting material. Sanguinarine (**4**) and chelerythrine (**5**) could be formed by double cyclizations of an intermediate followed by deprotonation (Chart 4).

(+)-Chelidonine (**1**) was oxidized with *m*-chloroperbenzoic acid to give a separable mixture of the N-oxides in 5.7 : 1 ratio. There are two main conformational types of *cis*-fused



22 : $R^1+R^2=CH_2$
23 : $R^1+R^2=CH_3$

Chart 4



anti–cis *syn–cis*

Fig. 1

hexahydrobenzo[*c*]phenanthridines (*syn–cis* and *anti–cis*)[10] (Fig. 1). In (+)-chelidonine (**1**), which has *anti–cis* and twist half-chair in the B and C rings, $J_{11,12\alpha}$ and $J_{11,12\beta}$ are 4.4 and 0 Hz, respectively,[11] while in (+)-chelidonine (**1**) O-acetate, which has *syn–cis* and twist half-chair in the B and C rings, $J_{11,12\alpha}$ and $J_{11,12\beta}$ are 5.0 and 11.3 Hz, respectively.[11] The coupling constants, $J_{11,12\alpha}$ and $J_{11,12\beta}$ are 7.0 and 2.0 Hz, respectively, in the major N-oxide (**24**). The corresponding coupling constants are 5.5 and 2.5 Hz in the minor N-oxide (**25**). These coupling constants allow assignment of the *anti–cis* form for both **24** and **25** (Fig. 1). As described below, equatorial and axial N-methyl groups were assigned to **24** and **25**, respectively. In the ^{13}C-NMR spectrum of the N-oxide (**25**), the N-methyl signal was observed at δ 56.39 while that in the N-oxide (**24**) appeared at δ 58.82. The axial N-methyl group (Fig. 1, *anti–cis*, R = H) was assigned to **25** on the basis of an upfield shift of the N-methyl signal in the ^{13}C-NMR spectrum of **25**. This upfield shift arises from a steric interaction between the axial N-methyl group and the hydroxyl group at 11-C. The difference in chemical shift at 11-C between **24** (δ 73.96) and **25** (δ 80.20) can be explained by a steric interaction between the hydroxyl group at 11-C and the axially oriented substituent at the N atom. In the ^1H-NMR spectrum, the signal due to 4-H in the N-oxide (**25**) appeared at lower field (δ 7.48) than the corresponding signal of the N-oxide (**24**) (δ 7.01). The 4-H and the oxygen atom on the N atom lie on about the same plane spatially in the conformation assigned for **25**, and 4-H may be deshielded by a lone pair of electrons on the oxygen anion in an equatorial orientation. The orientation of the N-methyl group was also supported by nuclear Overhauser enhancement (NOE) experiments. Saturation of the N-methyl frequency (δ 3.08) of **25** produced a 13% increase in the intensity of the line due to the equatorial 6-H proton at δ 5.0 (the low-field proton), but no change in the signals due to the axial 6-H and 4b-H protons (δ 4.61 and δ 4.82), while irradiation of the N-methyl resonance (δ 3.34) of **24** resulted in 5, 6, and 5% enhancements of the axial 6-H (δ 4.61), the equatorial 6-H (δ 4.87), and the axial 4b-H (δ 5.03), respectively. These positive enhancements arise from the fact that the three protons are gauche with respect to the equatorial N-methyl group in **24**.

The major N-oxide of (+)-chelidonine (**24**) was heated in a sealed pressure vessel at 185—215 °C and 3—5 mmHg to afford three products, which were separated by PTLC over silica gel. The first (23.8% yield) was spectrally identical with a sample of dihydrosanguinarine

(**22**). The second product (11.5% yield) from the pyrolysis had the molecular formula $C_{20}H_{19}NO_6$, corresponding to that of the starting N-oxide. The IR spectrum showed a band at 3170 cm^{-1}. The structures **26**, **27**, and **28** could be considered for this material (Chart 5).[12]

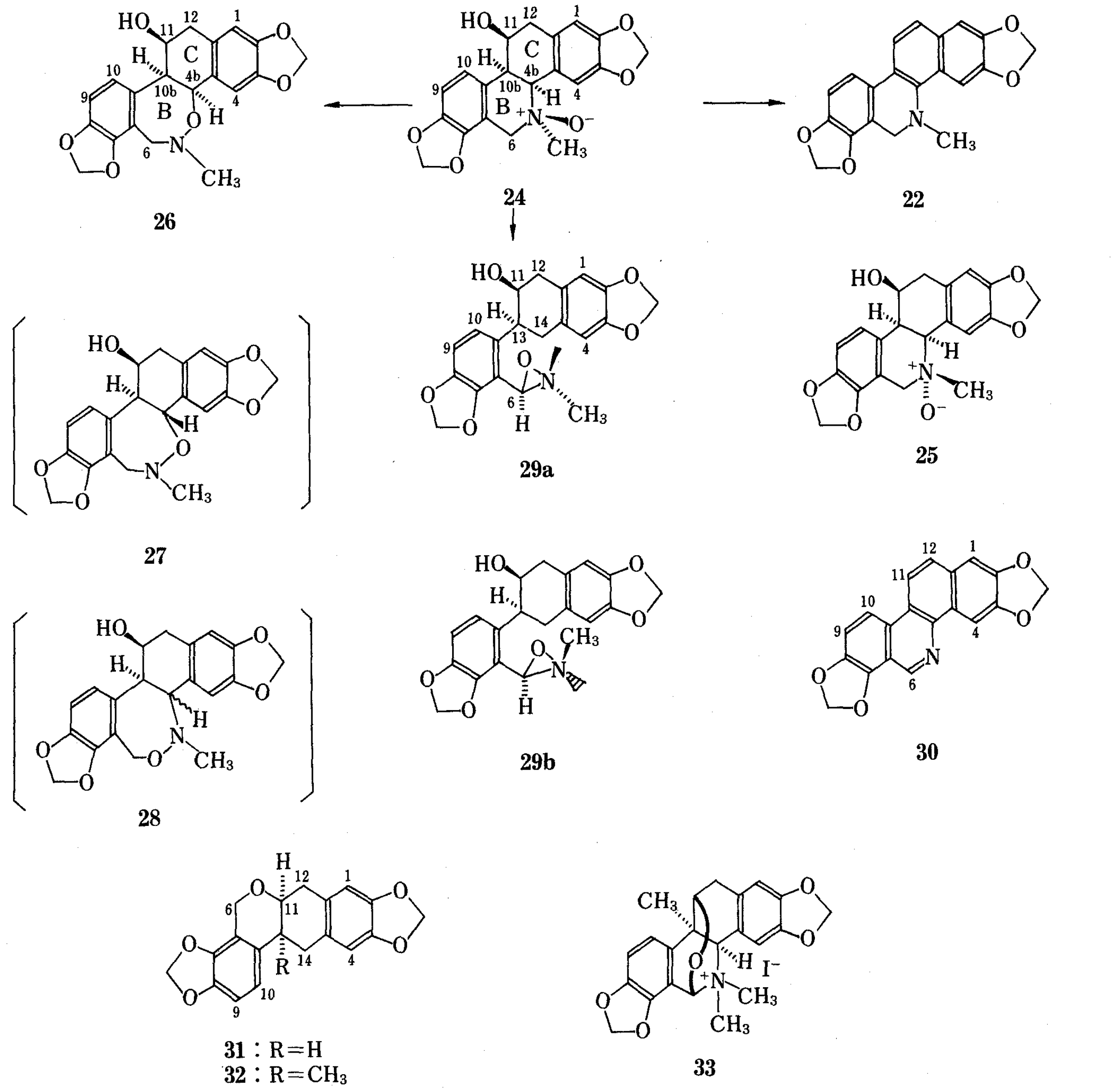


Chart 5

The compounds having these structures can be produced by the Meisenheimer rearrangement of the N-oxide (**24**). In the ^{1}H-NMR spectrum, signals due to methylene at position 6 adjacent to the nitrogen atom rather than oxygen appeared as doublets at δ 4.13 and 4.02 ($J=16.0$ Hz). The signal of 4b-H was observed as a doublet at δ 5.10 ($J=8.0$ Hz). The corresponding proton adjacent to the nitrogen atom in (+)-chelidonine (**1**) appeared as a doublet at δ 3.56 ($J=2.2$ Hz). Structure **28** was excluded by the chemical shifts of 6-H and 4b-H. Structure **26** having a *cis* B/C fusion was assigned to this product to explain the large amount of intramolecular hydrogen bonding showing up in the IR spectrum (in $CHCl_3$) between 3300 and 3000 cm^{-1}. The structure (**26**) having the *cis* fusion rather than **27** was also supported by NOE experiments. Irradiation of 4b-H at δ 5.10 resulted in a 10% enhancement of the signal of 10b-H at δ 3.43, while irradiation of 10b-H produced a 25% enhancement of that of 4b-H. The coupling constant observed between 10b-H and 4b-H is relatively large (8.0 Hz). The corresponding coupling constant in (+)-chelidonine (**1**) having the B/C *cis* fused ring is

2.2 Hz. The difference observed here can be attributed to a difference in dihedral angle. In the structure **26**, the B ring (seven-membered ring) might be twisted to avoid a nonbonded interaction between 6-H and 4b-H. The third product (17.5% yield) obtained from the pyrolysis of **24** had the formula $C_{21}H_{19}NO_6$ and showed a broad band at 3500—3100 cm^{-1} in the IR spectrum. The ^1H- and ^{13}C-NMR spectra of the product displayed two sets of signals in a ratio of 1.3 : 1. The ^{13}C-NMR spectrum exhibited two types of methine carbons at lower field (δ 86.93 and 90.40). The ^1H-NMR spectrum showed no methylene protons neighboring the nitrogen atom and one proton in total at δ 5.42 and 5.76 as a singlet instead of the methylene protons. The NMR spectral data verify the presence of an oxaziridine ring structure and suggest the diastereomeric nature of the pairs. Nitrogen inversion of oxaziridines is slow on the NMR time scale, both because the three-membered ring structure impedes nitrogen inversion and because of the presence of the electron-withdrawing oxygen.[13] Therefore of two isomers coexist in solution. In oxaziridines, the proton *cis* to the lone pair on nitrogen is preferentially deshielded.[14] The methine proton in the oxaziridine ring of this product resonates at δ 5.42 and 5.76 in the major and minor isomers, respectively. The *trans*- and *cis*-oxaziridine configurations (**29a** and **29b**) were assigned for the major and minor isomers, respectively. This was also supported by NOE experiments. The signals of the N-methyl group and 6-H of the two isomers are well separated from one another in the ^1H-NMR spectrum of **29**, and NOE experiments can be done between them. Saturation of the major line of the N-methyl group (δ 2.94) resulted in a 19% increase in the intensity of the

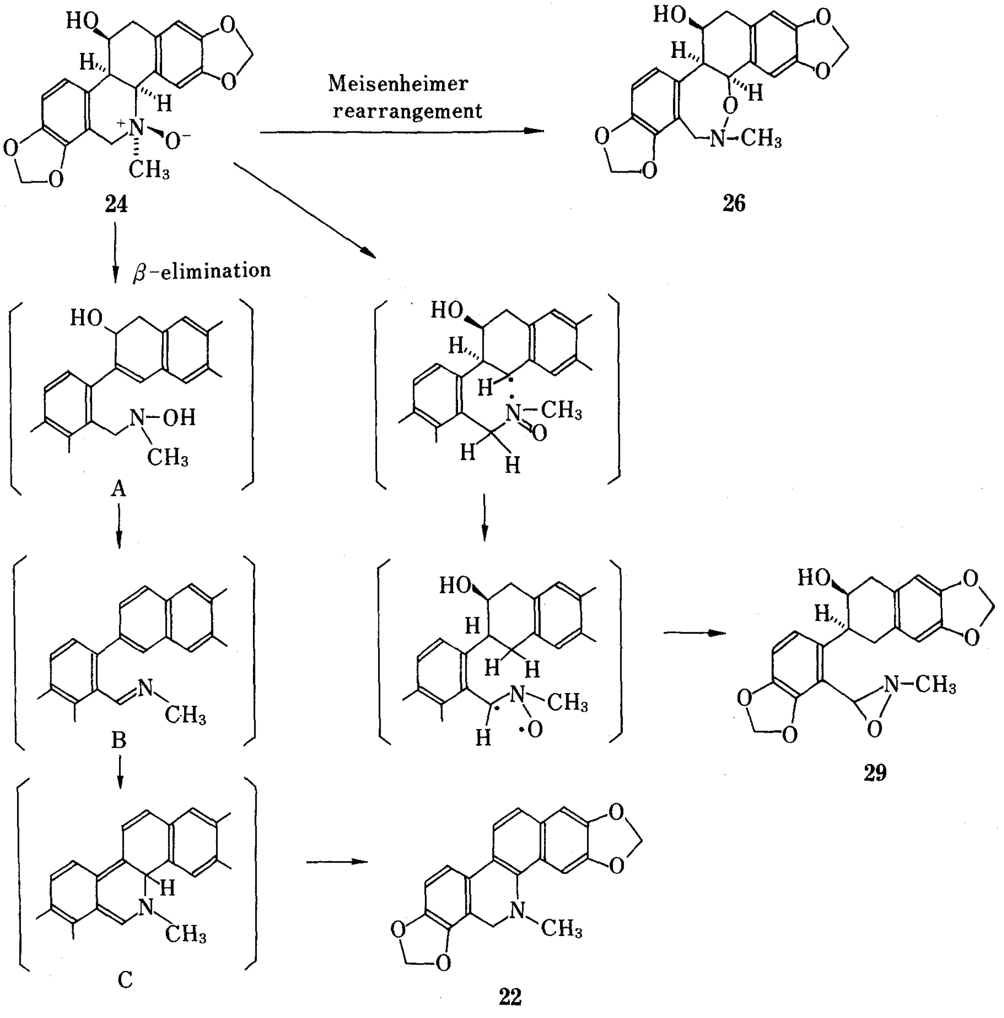


Chart 6

major 6-H signal (δ 5.42). Saturation of the major 6-H signal produced a 9% enhancement of the major N-methyl signal, while saturations of the N-methyl signal and the 6-H signal (δ 2.76 and δ 5.76) in the minor lines produced a negligible enhancement of the minor 6-H and N-methyl signals, respectively. This showed that the N-methyl group and the 6-H are close together in the major isomer.

A probable mechanism for formation of **22** from the N-oxide (**24**) is shown in Chart 6. An intermediate (A) formed by β elimination of the N-oxide (**24**) loses water to produce intermediate (B), which subsequently undergoes cyclization *via* a 6π-electrocyclic ring closure[15)] to give intermediate (C), which then undergoes a [1, 5]-hydrogen shift to give dihydrosanguinarine (**22**). Compound **26** would be produced by Meisenheimer rearrangement. The oxaziridine (**29**) may be formed by an initial cleavage into a radical pair followed by combination with a transfer of hydrogen as shown in Chart 6.

Pyrolysis of the minor N-oxide of (+)-chelidonine (**25**) at 185—210 °C *in vacuo* (3—5 mmHg) generated three products in very low yields of 1—2%. The first was identical with dihydrosanguinarine (**22**). The second had the parent ion and also a base peak at *m/z* 317 in its MS. The ^{1}H-NMR spectrum displays three one-proton singlets at δ 7.38, 8.71, and 9.84 and two pairs of *ortho* protons each as a doublet at δ 7.49 and 8.18 ($J=8.3$ Hz) and δ 7.88 and 8.34 ($J=8.5$ Hz). The second product was N-norsanguinarine (**30**) formed by loss of methane from **22**. The third product gave the parent ion at *m/z* 324 in the MS. The ^{1}H-NMR spectrum showed no N-methyl group and one methylene adjacent to oxygen, each as a doublet, at δ 4.87 and 4.98 ($J=16.0$ Hz). Structure **31** was assigned for this product by comparison of its ^{1}H-NMR spectrum with that of compound **32**, which has been obtained by Emde degradations of corynoloxine N-methyl iodide (**33**).[16)] Trace amount of N-norsanguinarine (**30**) and the compound (**31**) were also detected in the pyrolysis of **24**. Compounds **26** and **29** were not detected in the pyrolysis of the N-oxide (**25**). This may arise from the difference in the relative configuration of oxygen and nitrogen, as described above.

The formation of compound **9** or **16** from the N-oxide of the protopines followed by selective fission of the nitrogen to oxygen bond of **9** or **16** followed by reductive cyclization could occur to produce the secoberbines in nature. The present conversion of (+)-chelidonine N-oxide (**24**) into dihydrosanguinarine (**22**) could conceivably be a metabolic transformation in some plants.

Experimental

General Procedures——Melting points are uncorrected. MS were determined on a Hitachi M80 instrument at 75 eV. Isobutane gas was used to obtain the chemical ionization mass spectra. ^{1}H-NMR spectra and NOE experiments were performed on a Varian XL-200 (200.06 MHz) spectrometer. The concentrations of the compounds in the NOE samples were 0.03—0.04 M in $CDCl_3$ or CD_3OD. The sample was sealed under vacuum after four freeze-pump-thaw cycles. ^{13}C-NMR spectra were measured with a Varian XL-200 (50.31 MHz) spectrometer in a 10-mm tube. Chemical shifts are reported in parts per million relative to Me_4Si as an internal standard. The assignments of the carbon signals were made by the off-resonance decoupling and "insensitive nucleus enhanced by polarization transfer" (INEPT) methods and comparisons of chemical shifts. Chemical shift assignments with identical superscripts (asterisk and double asterisk) are interchangeable. Unless otherwise noted, the samples for NMR analyses were dissolved in $CDCl_3$. IR spectra were recorded on an EPI-G2 (Hitachi) spectrophotometer. TLC and PTLC were on Merck F-254 precoated silica gel plates.

Pyrolysis of Protopine N-Oxide (9)——Protopine N-oxide (**9**) (500 mg) was heated at 175—180 °C in a dry oven under a vacuum (20—30 mmHg) for 10 min. The crude product was separated into three fractions, I, II, and III in decreasing order of *Rf* values by PTLC (C_6H_6–Et_2O, 9 : 1). Compound **10** (300 mg, 60%) was obtained from fraction II as an oil. IR ($CHCl_3$): 1688 (C=O) cm^{-1}. ^{1}H-NMR (at 50 °C)[17)] δ: 2.51 (3H, s, N-CH_3), 2.85 (2H, m, 5-H), 3.06 (2H, m, 6-H), 4.06 (2H, br s, 13-H), 4.54 (2H, br s, 8-H), 5.93 and 5.94 (each 2H, s, $OCH_2O \times 2$), 6.68 (1H, s, 4-H), 6.89 (1H, s, 1-H), 6.74 and 6.77 (each 1H, d, $J=8.0$ Hz, 11- and 12-H). ^{13}C-NMR δ: 28.70 (5-C), 44.92 (N-CH_3), 46.83 (13-C), 62.19 (6-C), 64.60 (8-C), 101.28 and 101.43 ($OCH_2O \times 2$), 106.62 (1-C), 108.30 (11-C), 110.19 (4-C), 116.28 (8a-C), 124.70 (12-C), 129.85 (12a-C), 134,48 (14a-C),* 135.37 (4a-C),* 145.31 (2-C), 146.54 (9-C), 147.64 (10-

C), 149.18 (3-C), 202.23 (14-C). High-resolution MS *m*/*z*: Calcd for $C_{20}H_{19}NO_6$: 369.1212. Found: 369.1232. The hydrochloride had mp 190—210 °C dec. IR (Nujol): 2450—2100 ($\overset{+}{\mathrm{N}}$H), 1685 (C=O) cm^{-1}. *Anal.* Calcd for $C_{20}H_{19}NO_6 \cdot HCl$: C, 59.19; H, 4.97; N, 3.45. Found: C, 58.88; H, 4.96; N, 3.62.

Fraction III was recrystallized from $CHCl_3$–MeOH to give **13** (81 mg, 16%), mp 149—150 °C. IR (Nujol): 3180 (OH), 1695 (C=O) cm^{-1}. ^{1}H-NMR δ: 2.54 (3H, s, N-CH_3), 3.73 (2H, br s, 8-H), 4.18 (2H, br s, 13-H), 5.22 (1H, d, $J_{AX}=10.9$ Hz, $CH_X=C\underline{H}_AH_B$), 5.30 (1H, br s, OH), 5.52 (1H, d, $J_{BX}=17.3$ Hz, $CH_X=C\underline{H}_AH_B$), 5.95 and 6.03 (each 2H, s, $OCH_2O \times 2$), 6.61 and 6.72 (each 1H, d, $J=8.0$ Hz, 11- and 12-H), 7.03 (1H, s, 1-H), 7.10 (1H, dd, $J_{BX}=J_{AX}=$ 17.3 and 10.9 Hz, $C\underline{H}_X=CH_AH_B$), 7.22 (1H, s, 4-H), ^{13}C-NMR δ: 45.63 (13-C), 47.62 (N-CH_3), 57.35 (8-C), 101.04 and 101.85 ($OCH_2O \times 2$), 107.28 (1-C), 107.54 (11-C), 108.29 (4-C), 115.39 ($CH=\underline{C}H_2$), 117.92 (8a-C), 124.07 (12-C), 128.33 (12a-C), 131.12 (4a-C), 134.53 (14a-C), 135.84 ($\underline{C}H=CH_2$), 146.28 (9-C),* 146.91 (2-C),* 147.51 (10-C), 150.19 (3-C), 200.18 (14-C). MS *m*/*z*: (%, rel. int.): 369 (M^+, 3.9), 352 (16), 334 (19), 320 (20), 322 (21), 321 (23), 176 (29), 175 (100), 148 (22), 147 (33). *Anal.* Calcd for $C_{20}H_{19}NO_6$: C, 65.03; H, 5.19; N, 3.79. Found: C, 64.55; H, 5.10; N, 3.60.

Acetylation of **13** (20 mg) with acetic anhydride in pyridine under stirring at room temperature for 6 h and purification of the crude product by PTLC (C_6H_6–Et_2O, 2 : 1) gave the oily acetate **14** (10 mg, 45%). IR ($CHCl_3$): 1760 (C=O), 1685 (C=O) cm^{-1} ^{1}H-NMR δ: 1.94 (3H, s, $COCH_3$), 2.70 (3H, s, N-CH_3), 3.97 (2H, br s, 13-H), 4.50 (2H, br s, 8-H), 5.21 (1H, d, $J_{AX}=11.0$ Hz, $CH_X=C\underline{H}_AH_B$), 5.51 (1H, d, $J_{BX}=17.5$ Hz, $CH_X=CH_A\underline{H}_B$), 6.58 and 6.71 (each 1H, d, $J=8.0$ Hz, 11- and 12-H), 7.02 (1H, s, 4-H), 7.09 (1H, dd, J_{BX} and $J_{AX}=17.5$ and 11.0 Hz, $C\underline{H}_X=CH_AH_B$), 7.43 (1H, s, 1-H). MS *m*/*z* (%, rel. int.): 411 (M^+, 8.0), 352 (22), 176 (37), 175 (100), 149 (45), 148 (22), 147 (23).

Fraction I was recrystallized from $CHCl_3$–MeOH to afford **15** (20 mg, 4.6%), mp 159—162 °C. IR (Nujol): 3500 (OH) cm^{-1}. ^{1}H-NMR δ: 2.02 (3H, s, C-CH_3), 5.28 (1H, s, OH), 6.02 (2H, m, OCH_2O), 6.04 (2H, s, OCH_2O), 6.79 (2H, s, 5′- and 6′-H), 7.03 and 7.25 (each 1H, d, $J=8.2$ Hz, 3- and 4-H), 7.10 (1H, s, 5-H), 7.53 (1H, s, 8-H). ^{13}C-NMR δ: 12.43 (C-CH_3), 99.17 (3-C), 101.0 and 101.09 ($OCH_2O \times 2$), 103.68 (8-C), 106.49 (6′-C), 118.83 (5-C), 119.05 (2′-C), 119.46 (2-C), 120.37 (14a-C), 130.10 (4a-C), 131.39 (1′-C), 146.92 (4′-C),* 147.01 (3′-C),* 147.35 (7-C),** 147.89 (1-C), 147.95 (6-C).** MS *m*/*z* (%, rel. int.): 322 (M^+, 100), 176 (17). *Anal.* Calcd for $C_{19}H_{14}O_5$: C, 70.79; H, 4.38. Found: C, 70.85; H, 4.24.

Reduction of 10——Compound **10** (100 mg) was dissolved in 10% aqueous AcOH (80 ml) containing dilute HCl (1 ml) and zinc dust (500 mg) was added in portions to the stirred solution. The mixture was stirred at room temperature for one day, then filtered, made alkaline and extracted with ether. The crude product was subjected to PTLC (C_6H_6–Et_2O, 1 : 4) to give two products, **11** (upper *Rf*) and **12** (lower *Rf*), together with 32 mg (32%) of starting material.

Compound **11** (19 mg, 20%), mp 147—148 °C (MeOH–acetone). IR (Nujol): 3150 (OH) cm^{-1}. ^{1}H-NMR δ: 2.24 (3H, s, N-CH_3), 2.40—3.20 (4H, m, 5- and 6-H), 2.92 (1H, dd, $J=14.5$ and 3.5 Hz, 13-H), 2.97 (1H, dd, $J=14.5$ and 7.5 Hz, 13-H), 3.61 (1H, dd, $J=7.5$ and 3.5 Hz, 14-H), 4.50 and 4.62 (each 1H, d, $J=12.0$ Hz, 8-H), 5.94 and 5.99 (each 2H, m, $OCH_2O \times 2$), 6.55 (1H, s, 4-H), 6.61 and 6.69 (each 1H, d, $J=8.0$ Hz, 11- and 12-H), 6.69 (1H, s, 1-H). ^{13}C-NMR δ: 24.46 (5-C), 41.10 (13-C), 42.97 (N-CH_3), 47.30 (6-C), 54.93 (8-C), 66.50 (14-C), 100.83 and 101.04 ($OCH_2O \times 2$), 107.73 (1- and 11-C), 108.17 (4-C), 122.90 (8a-C), 123.39 (12-C), 127.49 (4a-C), 129.34 (14a-C), 132.60 (12a-C), 145.69 (9-C),* 146.10 (2-C),** 146.23 (3-C),** 146.34 (10-C).* CIMS *m*/*z*: 356 ($M^+ + 1$). *Anal.* Calcd for $C_{20}H_{21}NO_5$: C, 67.59; H, 5.96; N, 3.94. Found: C, 67.50; H, 5.87; N, 4.12. This material was identical with a sample of naturally occurring (+)-corydalisol (**11**).

Compound **12** (10 mg, 10%), mp 160—162 °C (acetone). ^{1}H-NMR δ: 2.33 (N-CH_3), 2.44—3.50 (4H, m, 5- and 6-H), 3.01 and 3.26 (each 1H, d, $J=16.0$ Hz, 13-H), 4.82 and 4.86 (each 1H, d, $J=16.0$ Hz, 8-H), 5.89 and 5.94 (each 2H, br s, $OCH_2O \times 2$), 6.57 (1H, s, 4-H), 6.56 and 6.67 (each 1H, d, $J=8.0$ Hz, 11- and 12-H), 6.88 (1H, s, 1-H). ^{13}C-NMR δ: 23.45 (5-C), 35.84 (N-CH_3), 36.06 (13-C), 45.60 (6-C), 59.22 (8-C), 86.78 (13a-C), 100.81 and 101.20 ($OCH_2O \times 2$), 106.65 (11-C), 107.09 (1-C), 108.48 (4-C), 116.88 (8a-C), 120.56 (12-C), 126.64 (4a-C), 128.66 (12a-C), 130.54 (14a-C), 142.24 (9-C), 145.52 (10-C), 146.38 (2-C), 147.01 (3-C). MS *m*/*z* (%, rel. int.): 353 (M^+, 3.8), 190 (13), 148 (100). *Anal.* Calcd for $C_{20}H_{19}NO_5$: C, 67.98; H, 5.42; N, 3.96. Found: C, 68.00; H, 5.35; N, 4.16.

Pyrolysis of 10——Compound **10** (60 mg) was pyrolyzed at 150 °C and 2 mmHg for 1 h. The product was subjected to PTLC (C_6H_6–Et_2O, 19 : 1) to give **15** (4 mg, 7.6%) together with 27 mg (45%) of starting material.

Preparation of Allocryptopine N-Oxide (16)——Allocryptopine (**7**) (100 mg) was dissolved in $CHCl_3$ (20 ml) and then *m*-chloroperbenzoic acid (65 mg) was added over 30 min. The mixture was allowed to stand at room temperature for 1 d. An additional amount of *m*-chloroperbenzoic acid (20 mg) was added and the mixture was left to stand at room temperature for 6 h. The solution was washed with 10% NaOH and then water. The organic layer was dried and the solvent was evaporated off. The residue was crystallized from MeOH–acetone to give **16** (90 mg, 86%), mp 147—148 °C (dec.). IR (Nujol): 3350 (br, OH, methanol of crystallization), 1682 (C=O) cm^{-1}. ^{1}H-NMR δ: 3.06 (3H, s, N-CH_3), 2.89 (1H, m, 5-H), 3.16—3.70 (2H, m, 5- and 6-H), 3.44 and 4.78 (each 1H, d, $J=15.5$ Hz, 13-H), 3.88 and 3.92 (each 3H, s, $OCH_3 \times 2$), 4.03 (1H, m, 6-H), 4.73 and 4.76 (each 1H, d, $J=14.0$ Hz, 8-H), 6.01 (2H, m, OCH_2O), 6.75 (1H, s, 4-H), 7.11 and 7.47 (each 1H, d, $J=8.0$ Hz, 11- and 12-H), 7.13 (1H, s, 1-H). ^{13}C-NMR (CD_3OD) δ: 31.22 (5-

C), 42.79 (13-C), 57.66 (N-CH_3), 56.40 and 61.23 ($OCH_3 \times 2$), 62.25 (6-C), 65.95 (8-C), 103.50 (OCH_2O), 110.89 (4-C), 112.23 (1-C), 115.75 (11-C), 124.01 (12a-C), 125.82 (8a-C), 129.16 (4a-C), 130.68 (12-C), 134.56 (14a-C), 148.78 (10-C), 150.38 (3-C), 152.35 (2-C), 153.06 (9-C), 202.58 (14-C). MS *m/z* (%, rel. int.): 385 (M^+, 58), 368 (47), 338 (58), 326 (100), 283 (39), 206 (31), 175 (41), 149 (80), 134 (41). *Anal.* Calcd for $C_{21}H_{23}NO_6 \cdot CH_3OH$: C, 63.30; H, 6.52; N, 3.36. Found: C, 63.27; H, 6.35; N, 3.38.

Pyrolysis of Allocryptopine N-Oxide (16)——Allocryptopine N-oxide **16** (622 mg) was heated at 124—129 °C in a dry oven in a vacuum (3—5 mmHg) for 9 min. The crude product was separated into two fractions by PTLC (C_6H_6–Et_2O, 9 : 1). The lower fraction was further subjected to PTLC (C_6H_6–MeOH, 19 : 1) to give **17** and **20** from the upper and lower bands on TLC, respectively.

Compound **17** (147 mg, 24%), mp 148—151 °C (MeOH). IR (Nujol): 1695 (C=O) cm^{-1}. ^1H-NMR δ: 2.51 (3H, s, N-CH_3), 2.84 (2H, m, 5-H), 3.04 (2H, m, 6-H), 3.83 and 3.84 (each 3H, s, $OCH_3 \times 2$), 4.09 (2H, br s, 13-C), 4.59 (2H, br s, 8-H), 5.95 (2H, s, OCH_2O), 6.70 (1H, s, 4-H), 6.88 and 7.02 (each 1H, d, J=8.0 Hz, 11- and 12-H), 6.91 (1H, s, 1-H). ^{13}C-NMR δ: 28.40 (5-C), 46.81 (13-C), 55.72 and 61.70 ($OCH_3 \times 2$), 62.27 (6-C), 65.17 (8-C), 101.45 (OCH_2O), 106.43 (1-C), 110.05 (4-C), 112.43 (11-C), 127.32 (12-C), 128.86 (8a-C), 129.51 (12a-C), 134.98 (14a-C),* 135.14 (4a-C),* 145.39 (2-C), 148.87 (10-C), 149.21 (3-C), 151.90 (9-C). MS *m/z* (%, rel. int.): 385 (M^+, 63), 368 (47), 326 (100), 283 (53), 206 (44), 149 (39), 134 (60). *Anal.* Calcd for $C_{21}H_{23}NO_6$: C, 65.44; H, 6.01; N, 3.63. Found: C, 65.34; H, 6.17; N, 3.56.

Compound **20**, amorphous (225 mg, 36%). IR ($CHCl_3$): 3600—3300 (OH), 1680 (C=O) cm^{-1}. ^1H-NMR δ: 2.51 (3H, s, N-CH_3), 3.84 (2H, br s, 8-H), 3.83 and 3.85 (each 3H, s, $OCH_3 \times 2$), 4.17 (2H, br s, 13-H), 5.21 (1H, dd, J_{AX} and J_{AB} = 10.9 and 1.1 Hz, $CH_X = C\underline{H}_A H_B$), 5.51 (1H, dd, J_{BX} and J_{BA} = 17.4 and 1.1 Hz, $CH_x = CH_A\underline{H}_B$), 6.03 (2H, s, OCH_2O), 6.85 (2H, s, 11- and 12-H), 7.03 (1H, s, 1-H), 7.18 (1H, dd, J_{BX} and J_{AX} = 17.4 and 10.9 Hz, $C\underline{H}_X = CH_A H_B$), 7.25 (1H, s, 4-H). ^{13}C-NMR δ: 46.12 (13-C), 47.31 (N-CH_3), 55.69 and 60.71 ($OCH_3 \times 2$), 57.09 (8-C), 101.82 (OCH_2O), 107.31 (1-C), 108.29 (4-C), 111.28 (11-C), 115.25 ($CH = \underline{C}H_2$), 126.97 (12-C), 127.60 (8a-C), 129.91 (12a-C), 131.17 (4a-C), 134.61 (14a-C), 136.02 ($\underline{C}H = CH_2$) 146.89 (2-C), 148.37 (10-C), 150.10 (3-C), 151.86 (9-C), 199.83 (14-C). MS *m/z* (%, rel. int.): 385 (M^+, 4.2), 368 (24), 351 (63), 350 (39), 338 (27), 337 (28), 336 (44), 192 (45), 175 (100), 147 (43).

The band with the higher *Rf* in PTLC (C_6H_6–Et_2O, 9 : 1) gave a third compound, which was recrystallized from MeOH–$CHCl_3$ to afford **21** (40 mg, 7.3%), mp 202—204 °C. IR ($CHCl_3$): 3545 (OH) cm^{-1}. ^1H-NMR δ: 2.08 (C-CH_3), 3.86 and 3.92 ($OCH_3 \times 2$), 5.22 (OH), 6.04 (2H, s, OCH_2O), 6.89 and 7.02 (each 1H, d, J=8.4 Hz, 5′- and 6′-H), 7.04 and 7.25 (each 1H, d, J=8.3 Hz, 3- and 4-H), 7.10 (1H, s, 5-H), 7.53 (1H, s, 8-H). ^{13}C-NMR δ: 13.19 (C-CH_3), 55.74 and 60.20 ($OCH_3 \times 2$), 99.17 (3-C), 101.0 (OCH_2O), 103.68 (8-C), 110.27 (6′-C), 118.83 (5-C), 120.35 (1a-C), 126.20 (5′-C), 126.54 (4-C), 129.11 (4a-C), 147.34 (7-C), 147.76 (4′-C),* 148.08 (6-C),* 152.76 (2′-C). MS *m/z* (%, rel. int.): 338 (M^+, 100), 323 (19). *Anal.* Calcd for $C_{20}H_{18}O_5$: C, 70.99; H, 5.36. Found: C, 70.77; H, 5.25.

Reduction of 17——Compound **17** (98 mg) was dissolved in 10% aqueous AcOH (40 ml) containing conc. HCl (0.5 ml) and zinc dust (500 mg) was added to the stirred solution. The mixture was stirred overnight. An additional amount of zinc dust (300 mg) was added and the mixture was gently refluxed for 30 min. The solution was filtered, made alkaline, and then extracted with ether. The organic layer was dried and evaporated. The crude product was subjected to PTLC (MeOH) to give products **18** (upper band) and **19** (lower band). Compound **18** (60 mg, 60%), mp 105—107 °C. IR ($CHCl_3$): 3400—3000 (OH) cm^{-1}. ^1H-NMR δ: 2.20 (3H, s, N-CH_3), 2.40—3.20 (6H, m, 5-, 6-, and 13-H), 3.60 (1H, dd, J=7.0, 3.5 Hz, 14-H), 3.85 and 3.89 (each 3H, s, $OCH_3 \times 2$), 4.47 and 4.76 (each 1H, d, J=11.4 Hz, 8-H), 5.93 (2H, br s, OCH_2O), 6.54 (1H, s, 4-H), 6.69 (1H, s, 1-H), 6.82 and 6.83 (each 1H, d, J=8.5 Hz, 11- and 12-H). ^{13}C-NMR δ: 24.69 (5-C), 41.59 (13-C), 43.11 (N-CH_3), 47.53 (6-C), 55.10 (8-C), 55.81 and 61.85 ($OCH_3 \times 2$), 66.39 (14-C), 100.77 (OCH_2O), 107.69 (1-C), 108.16 (4-C), 111.80 (9-C), 126.03 (10-C), 127.84 (4a-C), 129.77 (14a-C), 132.02 (12a-C), 135.43 (8a-C), 146.10 (2-C),* 146.22 (3-C),* 147.51 (10-C), 151.20 (9-C). CIMS *m/z*: 372 ($M^+ + 1$). This material was identified by direct comparison with an authentic sample of **18**.9)

Compound **19**, amorphous (1.5 mg, 1.5%). ^1H-NMR δ: 2.39 (3H, s, N-CH_3), 2.50—3.50 (6H, m, 5-, 6-, and 13-H), 3.88 (6H, s, $OCH_3 \times 2$), 4.92 (2H, br s, 8-H), 5.92 (2H, s, OCH_2O), 6.61 (1H, s, 4-H), 6.82 (2H, br s, 11- and 12-H), 6.86 (1H, s, 1-H). MS *m/z* (%, rel. int.): 369 (M^+, 5.6), 190 (73), 164 (100), 149 (52).

Pyrolysis of 17——Compound **17** (30 mg) was pyrolyzed at 150 °C and 2—3 mmHg for 1 h. The product was subjected to PTLC (C_6H_6–Et_2O, 19 : 1) to give **21** (3 mg, 11%) together with 18 mg (60%) of the starting material.

Photolysis of Protopine N-Oxide (9)——A solution of **9** (100 mg) in MeOH (100 ml) was irradiated with a high-pressure mercury lamp under nitrogen with cooling in running water for 2.5 h. The solvent was evaporated off and the residue was subjected to PTLC (C_6H_6–Et_2O, 9 : 1) to afford **10** (24 mg, 24%, upper *Rf*) and an orange colored product (lower *Rf*), which was reduced with $NaBH_4$ in MeOH to give **22** (1 mg, 1%); this was identified by direct comparison with a sample of dihydrosanguinarine (**22**). Some starting material (37 mg) was recovered.

Photolysis of Allocryptopine N-Oxide (16)——Irradiation of a solution of **16** (100 mg) in MeOH (100 ml) and work-up as described above for **9** provided two products, **17** (15 mg, 15%) and a yellow colored product which was reduced with $NaBH_4$ in MeOH to give **23**(2 mg, 2%); this was identical in terms of IR and ^1H-NMR spectra with dihydrochelerythrine (**23**). Some starting N-oxide (33 mg) was recovered.

Preparations of (+)-Chelidonine N-Oxides (24 and 25)——A solution of (+)-chelidonine (**1**, 2 g) in $CHCl_3$

(100 ml) was added to a solution of *m*-chloroperbenzoic acid (1.28 g) in $CHCl_3$ (150 ml) over a 40 min period. The mixture was allowed to stand at room temperature for 1 h and then washed with 1% NaOH solution followed by saturated aqueous NaCl. The organic layer was dried and evaporated. The residue was chromatographed on a silica gel column with ether–methanol with increasing MeOH content as the eluent to give a major component (**24**, 1.737 g, 83%) followed by a minor product contaminated with the major component. The latter was purified by PTLC (Et_2O–MeOH, 4 : 1) to afford the pure second component (**25**, 303 mg, 14.5%). The major N-oxide (higher *Rf*) **24**, mp 194—195 °C (MeOH–AcOEt). IR (Nujol): 3620, 3300 (br), and 3190 (br) (OH) cm^{-1}. ^1H-NMR (CD_3OD) δ: 3.14 (1H, dd, $J_{12\alpha,12\beta}=18.5$ Hz, $J_{11,12\beta}=2.0$ Hz, 12β-H), 3.31 (1H, dd, $J_{12\alpha,12\beta}=18.5$ Hz, $J_{11,12\alpha}=7.0$ Hz, 12α-H), 3.34 (3H, s, N-CH_3), 3.59 (1H, t, $J=5.0$ Hz, 10b-H), 4.27 (1H, ddd, $J=7.0$, 5.0, 2.0 Hz, 11-H), 4.61 and 4.87 (each 1H, d, $J=16.0$ Hz, 6-H), 5.03 (1H, d, $J=5.0$ Hz, 4b-H), 5.98 and 6.04 (each 1H, d, $J=1.0$ Hz, OCH_2O), 6.00 (2H, s, OCH_2O), 6.73 (1H, s, 1-H), 6.86 and 6.94 (each 1H, d, $J=8.0$ Hz, 9- and 10-H), 7.01 (1H, s, 4-H). ^{13}C-NMR(CD_3OD) δ: 40.33 (12-C), 43.49 (10b-C), 58.82 (N-CH_3), 66.99 (6-C), 67.31 (4b-C), 73.96 (11-C), 102.83 and 103.08 ($OCH_2O \times 2$), 109.31 (1-C),* 110.02 (9-C),* 112.74 (6a-C), 113.40 (4-C), 120.44 (4a-C), 121.93 (10-C), 128.66 (1a-C), 134.77 (10a-C), 145.31 (7-C), 146.89 (3-C), 147.40 (2-C), 150.83 (8-C). CIMS *m/z* 370 ($M^+ + 1$). *Anal.* Calcd for $C_{20}H_{19}NO_6 \cdot CH_3OH$: C, 62.83; H, 5.77; N, 3.49. Found: C, 62.73; H, 5.58; N, 3.57.

The minor N-oxide **25**, mp 178—180 °C (MeOH–AcOEt). IR (Nujol): 3500—2600 (br) (OH) cm^{-1}. ^1H-NMR (CD_3OD) δ: 3.00 (1H, dd, $J_{12\alpha,12\beta}=18.0$ Hz, $J_{11,12\beta}=2.5$ Hz, 12β-H), 3.08 (3H, s, N-CH_3), 3.16 (1H, dd, $J_{12\alpha,12\beta}=18.0$ Hz, $J_{11,12\alpha}=5.5$ Hz, 12α-H), 3.42 (1H, dd, $J=6.0$, 3.0 Hz, 10b-H), 4.42 (1H, ddd, $J=5.5$, 3.5, 2.5 Hz, 11-C), 4.61 and 5.00 (each 1H, d, $J=14.5$ Hz, 6-H), 4.82 (1H, d, $J=6.0$ Hz, 4b-H), 6.02 and 6.04 (each 1H, d, $J=1.0$ Hz, OCH_2O), 6.00 (2H, s, OCH_2O), 6.72 (1H, s, 1-H), 6.86 and 6.93 (each 1H, d, $J=8.0$ Hz, 11- and 12-H), 7.48 (1H, s, 4-H). ^{13}C-NMR (CD_3OD) δ: 39.65 (12-C), 45.34 (10b-C), 56.39 (N-CH_3), 64.34 (4b-C), 69.09 (6-C), 80.20 (11-C), 102.64 and 102.96 ($OCH_2O \times 2$), 109.06 (1-C),* 109.86 (9-C),* 112.58 (4-C), 113.67 (6a-C), 121.82 (4a-C), 122.13 (10-C), 131.25 (1a-C),** 131.44 (10a-C),** 145.60 (7-C), 147.09 (3-C), 147.94 (2-C), 150.56 (8-C). CIMS *m/z*: 370 ($M^+ + 1$). *Anal.* Calcd for $C_{20}H_{19}NO_6 \cdot 2/5CH_3OH$: C, 64.10; H, 5.43; N, 3.66. Found: C, 63.83; H, 5.15; N, 3.71.

Pyrolysis of (+)-Chelidonine N-Oxide (24)——(+)-Chelidonine N-oxide (**24**, 200 mg) was heated at 185—215 °C and 2—3 mmHg. The decomposition residue was subjected to PTLC (C_6H_6) to afford three products. The uppermost fraction was crystallized from methanol to give **22** (43 mg, 23.8%), mp 194—195 °C, spectrally identical with a sample of dihydrosanguinarine (**22**).

The fraction with next highest *Rf* gave **26** (23 mg, 11.5%), mp 208—210 °C (MeOH). IR ($CHCl_3$): 3300—3000 cm^{-1}. ^1H-NMR δ: 2.63 (3H, s, N-CH_3), 2.88 (1H, br d, $J=15.5$ Hz, 12-H), 2.98 (1H, dd, $J=15.5$, 2.5 Hz, 12-H), 3.43 (1H, dd, $J=8.0$, 2.0 Hz, 10b-H), 4.00 (1H, m, 11-H), 4.02 and 4.13 (each 1H, d, $J=16.0$ Hz, 6-H), 5.10 (1H, d, $J=8.0$ Hz, 4b-H), 5.98 and 6.00 (each 2H, m, $OCH_2O \times 2$), 6.66 (1H, s, 1-H), 6.76 and 6.78 (each 1H, d, $J=8.0$ Hz, 9- and 10-H), 7.02 (1H, s, 4-H). High-resolution CIMS $C_{20}H_{20}NO_6$ ($M^+ + 1$): Calcd: 370.1351. Found: 370.1320. MS *m/z* (%, rel. int.): 369 (M^+, 28), 351 (33), 334 (39), 305 (45), 275 (100).

The fraction with the lowest *Rf* afforded **29** (35 mg, 17.5%), mp 219—221 °C ($CHCl_3$–acetone). IR (Nujol): 3500—3100 (br, OH) cm^{-1}. ^1H-NMR δ: major and minor signals 2.94 and 2.76 (3H in total, s, N-CH_3), 2.70—3.28 (5H in total, m, 12-, 13-, and 14-H), 5.42 and 5.76 (1H in total, s, 6-H), 6.66 and 6.64 (1H in total, s, 4-H), 6.75 and 6.63 (1H in total, d, $J=8.0$ Hz, 9- or 10-H), 6.83 and 6.71 (1H in total, d, $J=8.0$ Hz, 9- or 10-H). ^{13}C-NMR δ: major and minor lines 34.30 and 34.74 (14-C), 36.10 and 36.54 (12-C), 42.64 and 41.65 (N-CH_3 and 13-C), 69.11 and 70.27 (11-C), 86.93 and 90.40 (6-C), 101.33 and 100.58 ($OCH_2O \times 2$), 108.15 (1-C),* 108.30 (4-C),* 108.81 and 108.61 (9-C), 114.85 and 115.33 (6a-C), 120.87 and 120.45 (10-C), 125.57 and 125.55 (4a-C), 127.88 and 128.04 (14a-C), 135.14 and 135.01 (10a-C), 144.08 (7-C),** 145.87 and 145.80 (3-C),** 146.21 and 146.25 (2-C),** 146.53 and 146.28 (8-C). High-resolution MS $C_{20}H_{19}NO_6$ (M^+): Calcd: 369.1210. Found: 369.1174. MS *m/z* (%, rel. int.): 369 (M^+, 6.6), 353 (39), 323 (100), 275 (44), 188 (44), 175 (37), 162 (57), 148 (46), 135 (61).

Pyrolysis of (+)-Chelidonine N-Oxide (25)——(+)-Chelidonine N-oxide (**25**, 100 mg) was heated at 185—210 °C and 2—3 mmHg. The decomposition residue was subjected to PTLC (C_6H_6–Et_2O, 9 : 1) to give trace amounts of three products (about 1—2 mg). The first with the highest *Rf* was spectrally identical with dihydrosanguinarine (**22**). The second product with the lowest *Rf* was spectrally identical with N-norsanguinarine (**30**). ^1H-NMR δ: 6.15 and 6.32 (each 2H, s, OCH_2O), 7.38 (1H, s, 1-H), 7.49 and 8.18 (each 1H, d, $J=8.3$ Hz, 11- and 12-H), 7.88 and 8.34 (each 1H, d, $J=8.5$ Hz, 9- and 10-H), 8.71 (1H, s, 4-H), 9.48 (1H, s, 6-H). MS *m/z* (%, rel. int.): 317 (M^+, 100). The third product with the middle *Rf* was crystallized from MeOH to give **31**, mp 200—201 °C. ^1H-NMR δ: 2.81 (1H, m, 13-H), 2.82 (1H, br d, $J=12.5$ Hz, 14-H), 2.83 (1H, dd, $J=12.5$, 6.5 Hz, 14-H), 3.01 (1H, dd, $J=17.5$, 1.5 Hz, 12-H), 3.18 (1H, dd, $J=17.5$, 5.0 Hz, 12-H), 4.09 (1H, m, 11-H), 4.87 and 4.98 (each 1H, d, $J=16.0$ Hz, 6-H), 5.95 and 5.98 (each ABq, $J=1.0$ Hz, $OCH_2O \times 2$), 6.56 (1H, s, 1-H), 6.63 (1H, s, 4-H), 6.62 and 6.75 (each 1H, d, $J=8.0$ Hz, 9- and 10-H). MS *m/z* (%, rel. int.): 324 (M^+, 37) 176 (62), 148 (100).

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