An Insecticidal Alkaloid, Cocculolidine from
*Cocculus trilobus* DC.

Part II. The Structure of Cocculolidine

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Received November 5, 1966

An insecticidal alkaloid, cocculolidine was extracted from fresh leaves of *Cocculus trilobus* DC. Von Braun reaction and a novel acid catalyzed degradation showed that this alkaloid had the same skeleton with those of erythrina alkaloids. Structure (I) was finally assigned to cocculolidine, being identified as a new lactone erythrina alkaloid containing \(\alpha,\beta\)-unsaturated-\(\gamma\)-lactone. The mass spectra of I and dihydro-\(\beta\)-erythroidine were also discussed.

Cocculolidine is an alkaloid isolated from fresh leaves of *Cocculus trilobus* DC., and exhibits insecticidal activities for several insects. This report presents evidences which permit the assignment of the structure (I) for cocculolidine.

Cocculolidine, \(\text{C}_{15}\text{H}_{19}\text{O}_{3}\text{N}\), MW 261 (by mass spectrum), m.p. 144\(\sim\)146°C, \([\alpha]_D^{25}+237^\circ\) (c, 1.0 in CHCl\(_3\)), gave the corresponding mono-

hydrochloride, \(\text{C}_{15}\text{H}_{19}\text{O}_{3}\text{N HCl}\), m.p. 247\(\sim\)251°C (dec.). When cocculolidine was refluxed with excess methylidide in methanol, the methiodide, \(\text{C}_{15}\text{H}_{19}\text{O}_{3}\text{N CH,I}\), m.p. 261\(\sim\)264°C (dec.) was readily formed. Spectral data and functional group analysis demonstrated the presence of a methoxyl (3H at 3.3 p.p.m. as a singlet and by Zeisel's method), a trisubstituted ethylene group (1H at 5.7 p.p.m. as a multiplet), and an \(\alpha,\beta\)-unsaturated-\(\gamma\)-lactone (\(\nu_{\text{max}}\) (CHCl\(_3\)) 1760 and 1650 cm\(^{-1}\), \(\alpha_{\text{MeOH}}\) 215 m\(_{\mu}\), \(\varepsilon=12,700\) and 2H at 4.7 p.p.m. as a singlet). The base peak (M-58) in the mass spectrum of cocculolidine indicated the presence of cyclohexene ring having a methoxyl group, which was cleaved to give M-58 ion fragment and \(\text{CH}_3\text{O}—\text{CH}==\text{CH}_2\) by retro-Diels-Alder decomposition (see Fig. V).

The half-height width (24 c.p.s.) of the signal of the hydrogen on the carbon bearing the methoxyl group (1H at 4.1 p.p.m. as a multiplet) suggested that the hydrogen was axial and three or four hydrogens should be present on the two adjacent carbons.

Reduction of cocculolidine with sodium borohydride in methanol gave dihydrococculolidine (II), \(\text{C}_{15}\text{H}_{21}\text{O}_{3}\text{N}\), m.p. 121\(\sim\)121.5°C. The spectral data of II showed end absorption in UV; \(\nu_{\text{max}}\) (CHCl\(_3\)) 1775 cm\(^{-1}\), NMR 3.9 p.p.m. (1H as a doublet, J=9 c.p.s.) and 4.2 p.p.m. (1H as a quartet, J=9 and 3.8 c.p.s. (-CH-CH=O-C=O), clearly indicating that \(\alpha,\beta\)-unsaturated-\(\gamma\)-lactone in I was reduced to the saturated one. II was further hydrogenated on platinum oxide in glacial acetic acid to the fully saturated compound, tetrahydrococculolidine (III), \(\text{C}_{16}\text{H}_{23}\text{O}_{3}\text{N}\), m.p. 187\(\sim\)189°C, which showed no absorption in

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Thus, cocculolidine was concluded to be a tetracyclic compound.

Oxidation of II with potassium permanganate in the mixed solution of acetone and water produced oxo-dihydrococculolidine (IV), C_{15}H_{19}O_{4}N, m.p. 223-225°C. The newly formation of y-lactam in IV was indicated by the infrared spectrum, \( \nu_{\text{max}} (\text{KBr}) \) 1775 cm\(^{-1}\) (\( \gamma \)-lactone) and 1675 cm\(^{-1}\) (\( \gamma \)-lactam).

This observation permits to assume that one of two rings containing the nitrogen would be a five-membered one. Since reduction of IV with lithium aluminum hydride gave dihydrococculolidinol (V), C_{15}H_{25}O_{3}N, m.p. 93-95°C; \( \nu_{\text{max}} (\text{CHCl}_3) \) 3400 cm\(^{-1}\) (OH), which was also obtained by reduction of II with the same reagent, the possibility of skeletal rearrangement during the oxidation could be excluded. Potassium permanganate oxidation of III under the same condition with that for II gave also a \( \gamma \)-lactam derivative, oxo-tetrahydrococculolidine (VI), C_{15}H_{21}O_{4}N, m.p. 122-126°C, \( \nu_{\text{max}} (\text{CHCl}_3) \) 1775 cm\(^{-1}\) (\( \gamma \)-lactone) and 1675 cm\(^{-1}\) (\( \gamma \)-lactam).

The above data led to the following partial structures for cocculolidine.

\[ \text{CH}_3 \text{H}_4 \text{O} \text{H} \text{H} \text{H} \text{H} \]
\[ \text{(A)} \]
\[ \text{CH}_3 \text{H}_4 \text{O} \text{H} \text{H} \text{H} \]
\[ \text{(B)} \]
\[ \text{CH}_3 \text{H}_4 \text{O} \text{H} \text{H} \text{H} \text{H} \]
\[ \text{(C)} \]
\[ \text{CH}_3 \text{H}_4 \text{O} \text{H} \text{H} \text{H} \]
\[ \text{(D)} \]

The relationship between these partial structures to establish the full structure of cocculolidine was clarified by von Braun reaction of cocculolidine. Cocculolidine was refluxed with cyanogenbromide in chloroform to give C-15 cyanamide (VII), C_{15}H_{14}O_{2}N_{2}, m.p. 169-171.5°C; \( \nu_{\text{max}} (\text{CHCl}_3) \) 2205 cm\(^{-1}\) (\( \equiv \text{C}N \)), 1765 cm\(^{-1}\) (\( \alpha,\beta \)-unsaturated-\( \gamma \)-lactone) and 1670 cm\(^{-1}\) (C==C). The molecular formula, C_{15}H_{14}O_{2}N_{2} and the NMR spectrum (see Fig. 1), (7.0-7.6 p.p.m., 4H, m) showed occurrence of a drastic change during the reaction accompanied by dehydrobromination and loss of methanol, producing the aromatized compound. Moreover, the ultraviolet spectrum of C-15 cyanamide (see Fig. 3) showed the

![Fig. 1. NMR Spectrum of C-15 Cyanamide (p.p.m. in CDCl\(_3\)).](image)

![Fig. 2. NMR Spectrum of N-Acetyl C-14 Base (p.p.m. in CDCl\(_3\)).](image)

The above data led to the following partial structures for cocculolidine.

\[ \text{(A)} \]
\[ \text{(B)} \]
\[ \text{(C)} \]
\[ \text{(D)} \]

Among them, E was accepted as a corrected one and...
F was excluded because the five membered ring containing the nitrogen in cocculolidine should be formed by joining the nitrogen with the terminal carbon Ca or Cb. However, this is impossible in the structure F. The partial structure A was therefore extended to E.

The additional evidence supporting the partial structure E was obtained when cocculolidine could be transformed to the expected aromatized product (VIII) on treatment with conc. acid. Cocculolidine hydrochloride was heated in phosphoric acid at 170°C for 4 hours to give C₁₄ base (VIII), C₁₄H₁₅O₂N, m.p. 97~99°C. The spectral data, νₚₖₐₓₜ (KBr) 3300 cm⁻¹ and δᵣₑ₁₉ₒ_H₂ 255 m uplifting (ε=2570) and 275 m uplifting (ε=1000), showed the presence of secondary amine and sterically hindered o-substituted styrene group. Acetylation of VIII with acetic anhydride in benzene gave N-acetyl C₁₄ base (IX), C₁₆H₁₇O₃N, m.p. 175°C. In the NMR spectrum of IX, multiplet signals (7.0~7.4 p.p.m., 4H) was observed corresponding to four hydrogens on benzene ring. The formation of VIII could be reasonably understood confirming the partial structure E, which lost methanol first, followed by Hoffman type degradation as shown below.

The ultraviolet spectra of VII and VIII were shown in Fig. 3 compared with those of model compounds. They showed clearly the broad general absorption typical of sterically hindered o-substituted styrene, which was confirmed by obtaining phthalic acid after oxidation of VIII with potassium permanganate. These facts clearly indicated that the o-substituted benzene ring should conjugate to the carbon-carbon double bond of the α,β-unsaturated-γ-lactone in the similar manner to the chromophore of atropic acid. If the benzene ring was conjugated as the chromophore of cinnamic acid type, both VII and VIII might show quite similar absorption curves with that of a sterically hindered cinnamic acid derivative, α-(5,8-dimethyltetralydileiden)-propionic acid (see Fig. 3).
N-Formyl C_{14} base (X) which was obtained by the mild formylation\(^1\) of VIII was reduced with lithium aluminum hydride to give N-methyl C_{14} diol-base (XI), m.p. 117–119°C. The ultraviolet spectrum of XI also showed the broad general absorption typical of sterically hindered o-substituted styrene (see Fig. 3). From the above facts, the partial structure F was extended to the structure H or H'. However, the possibility of the latter was excluded since cocculolidine itself had no conjugated diene group. Subtracting H from the molecular formula of cocculolidine remained the unknown fragment C_{4}H_{8} which must be clarified. Since cocculolidine was a tetracyclic compound, and has no methyl group as shown in the NMR spectrum, the remained part was considered to be composed of four methylene groups. Moreover, in view of the fact that cocculolidine had a five membered ring containing the nitrogen, only two structures J and K remained as the probable structures for cocculolidine.

The conclusion that the structure J was correct could be obtained from the consideration of the NMR spectrum of C_{15} cyanamide (see Fig. 1). It showed two types of signals...
FIG. 4. The Relation of Degradates of Cocculolidine.

in the methylene region, one corresponding to four allylic and benzylic protons and the other to four protons on the carbons adjacent to the nitrogen, and no signals in the region of normal positions, indicating that C₁₅ cyanamide should be assigned to be structure L which was formed from the structure J. If C₁₅ cyanamide had the structure M which was formed from the structure K, the center of the three adjacent methylenes ought to show the signals in the normal methylene region. Thus, the structure K was excluded.

On the basis of these data, cocculolidine was reasonably assigned to the structure J (=the structure (I)). Cocculolidine is a new lactone erythrina alkaloid and also the second erythrina alkaloid found in the plant of Menispermaceae.⁵

⁵) A erythrina alkaloid, dihydroerysodine has been isolated from Coccolus laurifolius DC.; M. Tomita and H. Yamaguchi, Pharm. Bull., 4, 225 (1956).
Further evidence for the structure (I) was obtained by comparison of the mass spectrum of I with that of dihydro-β-erythroidine. The molecular weights of I and dihydro-β-erythroidine were confirmed by observing the parent peaks at 261 and 275 respectively. The mass spectra of both compounds showed same fragmentation pattern, suggesting that they had the same skeleton. They could be grouped into the two series of the fragments (Table I):

**TABLE I. MASS SPECTRA OF COCCULOLIDINE AND DIHYDRO-β-ERYTHROIDINE**

<table>
<thead>
<tr>
<th>Fragments</th>
<th>Cocculolidine</th>
<th>Dihydro-β-erythroidine</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/e</td>
<td>Strength</td>
<td>m/e</td>
</tr>
<tr>
<td>Group A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>261</td>
<td>14.9%</td>
</tr>
<tr>
<td>M-31</td>
<td>230</td>
<td>8.0%</td>
</tr>
<tr>
<td>M-32</td>
<td>229</td>
<td>24.0%</td>
</tr>
<tr>
<td>M-38</td>
<td>203</td>
<td>100%</td>
</tr>
<tr>
<td>Group B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>132</td>
<td>74.0%</td>
<td>132</td>
</tr>
<tr>
<td>118</td>
<td>92.4%</td>
<td>118</td>
</tr>
<tr>
<td>117</td>
<td>67.7%</td>
<td>117</td>
</tr>
<tr>
<td>91</td>
<td>64.5%</td>
<td>91</td>
</tr>
</tbody>
</table>

**Mass spectra**

FIG. 5. The Fragmentation Pattern of Cocculolidine and Dihydro-β-erythroidine.
first, group A, which was due to ions formed from both compounds by splitting same neutral fragments off; and secondly, group B, which was common ions having same mass numbers in both spectra.

**Group A peaks.** Both spectra had the M-31, M-32 and M-58 peaks suggestive the presence of cyclohexene ring containing methoxyl (ring A). The cocculolidine fragments, M-31 and M-32 occurred at m/e 230 and 229 as compared to m/e 244 and 243 in the case of dihydro-\(\beta\)-erythroidine, both of which were due to loss of methoxy and methanol. The base peaks at M-58 in both compounds\(^6\) were due to loss of CH\(_3\)OCH=CH\(_2\) fragments which were cleaved from the ring A by retro-Diels-Alder decomposition.

**Group B peaks.** Both spectra had m/e 132, 118, 117 and 91 fragments as the common ion fragments. The m/e 132 peak might be due to retro-Diels-Alder decomposition of the ring C of M-32 fragment accompanied by cleavage of the lactone fragment, being formed a methyl indolium ion. It was subsequently degraded to the m/e 117 fragment, confirmed by the occurrence of meta stable peak at m/e 105. The m/e 118 fragment might be due to splitting the ring C and lactone ring from M-32 fragment followed by loss of a hydrogen radical, which was further degraded to the m/e 91 fragment, tropylium ion.\(^7\)

**EXPERIMENTAL**

Melting points were uncorrected; ultraviolet spectra were measured with a Cary 14 spectrophotometer, and infrared spectra with a Hitachi EPI-2. NMR spectra of 60 Me were measured with a JNM-C-60 spectrometer in CDCl\(_3\) with tetramethylsilane as an internal standard.

\(^6\) It was noticeable that dihydroerysodine having the same skeleton revealed the base peak at M-59, which was due to loss of CH\(_3\)OCH=CH\(_2\) fragment and a hydrogen radical. Albert Mondon and Manfred Ehrhardt, *Tetrahedron Letters*, No. 23, 2557 (1966).

\(^7\) The similar fragmentation has been shown in the case of 2-methylindole. H. Budikiewicz, C. Djerassi and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds", 252 (1964).
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**Tetrahydrococculolidine (III).** A solution of 300 mg of II in 20 ml of acetic acid was hydrogenated at 31°C under atmospheric pressure in the presence of 60 mg of prereduced Adam's catalyst. A molar equivalent of hydrogen was absorbed in about 140 minutes. After removal of the catalyst by filtration, the filtrate was concentrated under reduced pressure and 5 ml of 5% hydrochloric acid solution was added to the residue. The solution was washed with ether to remove acetic acid, made alkaline with ammonia water, and then extracted with chloroform. The chloroform extract, on evaporation, gave 250 mg of white solid. The material was chromatographed on silicic acid with chloroform containing methanol as elution solvent. The fraction eluted with chloroform containing 10% of methanol, on evaporation, gave 100 mg of white plates, m.p. 187-188°C. Recrystallization from carbon tetrachloride gave white needles, m.p. 187-189°C. $\nu_{\text{max}}$ (KBr) 1765 cm$^{-1}$. NMR (p.p.m. in CDCl$_3$): 3.4 (3H as a ringlet, $\text{-OCH}_3$), 3.5 (1H as a multiplet, $\text{-CH-O-}$), 3.9 (1H as a doublet, $J=9$ c.p.s.) and 4.2 (1H as a quartet, $J=9$ and 9.3 c.p.s.) ($\text{-CH-CH}_2\text{-O-CO-}$). Anal. Found: C, 67.32; H, 8.56; N, 5.32. Calcd. for C$_{15}$H$_{23}$O$_3$N: C, 67.89; H, 8.74; N, 5.28%.

**Dihydrococculolidineol (V).** A solution of II in dry dioxane (1 g in 50 ml) was refluxed with 600 mg of lithium aluminum hydride for 1 hour. The excess reagent was then decomposed with cold water. The aqueous solution was extracted with chloroform. The chloroform extract, on evaporation under reduced pressure, gave 500 mg of oily product. This material was chromatographed on silicic acid with chloroform containing methanol. The fraction eluted with chloroform containing 10% of methanol, on evaporation, gave 350 mg of semi-solid, m.p. 78-84°C. This was recrystallized from n-hexane-methanol to give colorless prisms, m.p. 78-84°C. $\nu_{\text{max}}$ (CHCl$_3$) 3400 cm$^{-1}$. Anal. Found: C, 67.32; H, 8.56; N, 5.32. Calcd. for C$_{15}$H$_{25}$O$_3$N: C, 65.82; H, 9.33; N, 4.53.

**Oxodihydrococculolidine (IV).** To a solution of 200 mg of II and 500 mg of magnesium sulphate heptahydrate in 70 ml of acetone and 10 ml of water, a solution of 250 mg of potassium permanganate in 30 ml of water was added in ice-salt bath with stirring. Stirring was continued for further 35 minutes at room temperature. The excess reagent was destroyed with saturated solution of sodium sulphite in 5% sulphuric acid and the solvent was evaporated under reduced pressure. The concentrated solution was acidified with 5% hydrochloric acid and extracted with chloroform. The chloroform extract, on evaporation, gave 80 mg of oily material. The material was chromatographed on silicic acid with chloroform containing methanol. The fraction eluted with chloroform containing 1% of methanol, on evaporation, gave 40 mg of white solid. Recrystallization of this material from ethyl acetate gave 30 mg of colorless prisms, m.p. 223-225°C. $\nu_{\text{max}}$ (KBr) 1775 and 1675 cm$^{-1}$. Anal. Found: C, 64.68; H, 6.95; N, 5.21. Calcd. for C$_{16}$H$_{19}$O$_4$N: C, 64.96; H, 6.91; N, 5.05%.

**Transformation of IV to V.** This transformation was carried out by the analogous treatment as II. The melting point of this product was not depressed by admixture of V formed from II. This infrared spectrum was also identical with that of V.

**C-15 cyanamide (VII).** The reaction of 850 mg of I and 450 mg of cyanogenbromide in 30 ml of chloroform was refluxed for 1 hour. The cooled reaction mixture was then washed with 10 ml of 5% hydrochloric acid and 10 ml of 5% sodium bicarbonate. This material (360 mg) was chromatographed on silicic acid with chloroform. The first eluate, on evaporation, gave 20 mg of white solid, m.p. 169-171.5°C. $\nu_{\text{max}}$ (CHCl$_3$): 2205, 1765 and 1670 cm$^{-1}$. $\lambda_{\text{max}}$ (CH$_3$OH): 255 m$\mu$ ($\varepsilon=1850$) and 275 m$\mu$ ($\varepsilon=540$). NMR (p.p.m. in CDCl$_3$): 2.5-3.0 (4H as multiplet, $\text{-CH}_2\text{-N(CN)-CH}_2\text{-}$), 3.0-3.7 (4H as multiplet, $\text{-CH}_2\text{-N(CN)-CH}_2\text{-}$), 5.0 (2H as singlet, $\text{-C=C-CH}_2\text{-O-CO-}$), 7.0-7.6 (4H as multiplet, four protons on a benzene ring). Anal. Found: C, 70.76; H, 5.77; N, 10.87. Calcd. for C$_{15}$N$_2$O$_2$: C, 70.85; H, 5.55; N, 11.02%.

**C-14 base (VIII).** A solution of 330 mg of cocculolidine hydrochloride in 2 ml of 85% phosphoric acid was heated at 170°C for 4 hours. After the reaction mixture had been diluted with 10 ml of cold water, made alkaline with sodium hydroxide, and extracted with chloroform. The extract, on evaporation, gave 200 mg of white needles, m.p. 97-99°C. $\nu_{\text{max}}$ (KBr) 3300, 1730 and 1660 cm$^{-1}$. $\lambda_{\text{max}}$ (CH$_3$OH): 255 m$\mu$ ($\varepsilon=2570$) and 275 m$\mu$ ($\varepsilon=1000$). The picrate of VIII prepared in ethanol was recrystallized from the same solvent to give thin yellow prisms, m.p. 207-210°C (dec.). Anal. Found: C, 52.54; H, 3.91; N, 12.11. Calcd. for C$_{14}$H$_{13}$O$_2$N$_2$: C, 52.41; H, 3.86; N, 12.22%. 

$\gamma$(III). Anal. Found: C, 68.18; H, 8.30; N, 5.18; Calcd. for C$_{15}$H$_{21}$O$_3$N: C, 68.42; H, 8.04; N, 5.32%.
N-acetyl C-14 base (IX). A solution of 70 mg of VIII in 3 ml of benzene and 1 ml of acetic anhydride was refluxed for 15 minutes. The solvent and excess acetic anhydride was evaporated in reduced pressure. The residue was dissolved in chloroform and washed with dilute hydrochloric acid, sodium bicarbonate and water successively. The chloroform solution was dried and concentrated to afford 70 mg of colorless prisms. Recrystallization of this material from benzene gave 50 mg of colorless prisms, m.p. 173-175°C. \( \nu_{\text{max}} \) (CHCl₃) 1750 and 1630 cm⁻¹. NMR (p.p.m. in CDCl₃): 1.9 (3H as a singlet, \(-\text{N-COCH}_3\)), 2.5-2.9 (4H as multiplet, \(2\text{-C=C-CH}_2\)), 3.2-3.8 (4H as multiplet, \(-\text{CH}_2-\text{N(COCH}_3)\text{-CH}_2\)), 4.8 (2H as a singlet \(-\text{C=C-CH}_2\text{-O-CO-}\)), 7.0-7.40 (4H as multiplet, four protons on a benzene ring). Anal. Found: C, 71.34; H, 6.55; N, 5.03. Calcd. for C₁₆H₁₇O₃N: C, 70.83; H, 6.32; N, 5.16%.

N-formyl C-14 base (X). Acetic anhydride (1 ml) was added dropwise to a mixture of VIII and 3 ml of 85% formic acid. After the addition was complete, the mixture was stirred at room temperature for 1.5 hours, and then 10 ml of ice water was introduced. The resulting mixture was concentrated under reduced pressure. The residual aqueous solution was extracted with chloroform. The extract was washed with 5% sodium bicarbonate and 2.5% sulphuric acid. The washed chloroform layer was dried and concentrated to give 130 mg of semisolid. Recrystallization of this material from ethyl acetate gave 100 mg of colorless prisms, m.p. 163-165°C. \( \nu_{\text{max}} \) (KBr) 1735 and 1660 cm⁻¹. \( \lambda_{\text{max}} \) 298 m\( \mu \) (e=970) and 282 m\( \mu \) (e=1240). The infrared and ultraviolet spectra of the crystal was identical with those of authentic phthalic anhydride. The methyl ester of this acid was also recognized as dimethyl phthalate by gas chromatographic analysis (Conditions: Column, Silicon H. V. G. 2 m \( \times \) 4 mm; carrier gas, He; Column temperature, 175°C; Retention time, 25.2 minutes).

Permanganate oxidation of VIII. To a suspension of 180 mg of VIII and 10 ml of 10% sodium hydroxide a solution of 3% aqueous potassium permanganate was added until the permanganate color was no longer discharged on warming the reaction mixture to 80°C. The excess reagent was destroyed by the addition of saturated solution of sodium sulfite in 5% sulphuric acid. The solution was then extracted continuously with ether for 15 hours. After removal of the solvent, there remained 30 mg of crude acid. Sublimation of this material at atmospheric pressure gave 10 mg of white needles, m.p. 100-110°C. \( \nu_{\text{max}} \) (KBr) 1845, 1760, 1680 and 1580 cm⁻¹. \( \lambda_{\text{max}} \) 298 m\( \mu \) (e=970) and 282 m\( \mu \) (e=1240). The infrared and ultraviolet spectra of the crystal was identical with those of authentic phthalic anhydride. The methyl ester of this acid was also recognized as dimethyl phthalate by gas chromatographic analysis (Conditions: Column, Silicon H. V. G. 2 m \( \times \) 4 mm; carrier gas, 30/min. He; Column temperature, 175°C; Retention time, 25.2 minutes).

Acknowledgements. The authors are indebted to Prof. V. Boekelheide of University of Oregon for the generous supply of samples of erythroidine derivatives. The authors wish to express their thanks to Dr. H. Aoki of this faculty for helpful advices in the experimental work, Dr. S. Suzuki and Dr. K. Sasaki of the Institute of Physical and Chemical Research for the measurements of NMR spectra and Prof. Y. Hirata and Dr. H. Nakata of Nagoya University for the measurements of mass spectra. They are also grateful to Misses K. Nakane and M. Hamaji for microanalysis.