[Chem. Pharm. Bull.
29(2) 390—395 (1981)]

Studies on the Constituents of *Ailanthus altissima* SWINGLE. II.[1] Alkaloidal Constituents

TAICHI OHMOTO,* KAZUO KOIKE, and YOHKO SAKAMOTO

School of Pharmaceutical Science, Toho University,
Miyama, Funabashi, Chiba, 274, Japan

(Received September 2, 1980)

1-Acetyl-4-methoxy-β-carboline (I), canthin-6-one (VIIIa), 1-methoxycanthin-6-one (VIIIb), and canthin-6-one-3*N*-oxide (IXa), and three new alkaloids, 1-(2′-hydroxyethyl)-4-methoxy-β-carboline (IIa), 1-(1′,2′-dihydroxyethyl)-4-methoxy-β-carboline (IIIa), and 1-methoxycanthin-6-one-3*N*-oxide (IXb), were isolated from the root bark of *Ailanthus altissima* SWINGLE (Simaroubaceae). The structures of IIa, IIIa, and IXb were elucidated by spectroscopic and chemical studies.

Keywords——*Ailanthus altissima*; Simaroubaceae; alkaloid; β-carboline; canthinone; 1-acetyl-4-methoxy-β-carboline; 1-(2′-hydroxyethyl)-4-methoxy-β-carboline; 1-(1′,2′-dihydroxyethyl)-4-methoxy-β-carboline; 1-methoxycanthin-6-one-3*N*-oxide

In the previous paper,[1] we reported the isolation and structural elucidation of basic components in the bark of *Ailanthus altissima* SWINGLE (Simaroubaceae).

Further studies on the basic components of the root bark of *A. altissima* SWINGLE have been carried out in order to compare the components of different parts of the plant.

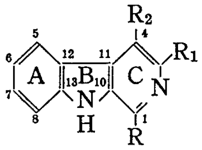
Seven compounds (I, IIa, IIIa, VIIIa, VIIIb, IXa, and IXb) have been isolated so far from the root bark of the plant. Of these compounds, I, VIIIa, VIIIb, and IXa were identified as 1-acetyl-4-methoxy-β-carboline, canthin-6-one, 1-methoxycanthin-6-one, and canthin-6-one-3*N*-oxide, respectively, which have already been reported in the literature,[1,2] but compounds IIa, IIIa, and IXb were found to be new compounds.

This paper deals with the isolation and characterization of these compounds.

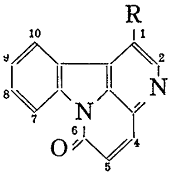
Continuous extraction of dried chips of the root bark of *A. altissima* was carried out with methanol, and the basic fraction, which showed 14 spots on a thin–layer chromatogram (TLC), was collected as described in the experimental section. The basic components were then fractionated by silica gel column chromatography, which yielded compounds I, VIIIa, VIIIb, and IXa, each in a pure state. Compounds IIa, IIIa, and IXb were further purified by preparative TLC.

Compound (I)[3] was obtained as pale yellow needles with mp 204—205°. The high resolution mass spectrum of compound (I) gave the molecular formula $C_{14}H_{12}N_2O_2$. In the infrared absorption (IR) spectrum. characteristic bands due to an imino group and a conjugated carbonyl group were observed at 3350, and 1670 cm^{-1}, respectively. The proton magnetic resonance (PMR) spectrum (Table I) suggested the presence of an acetyl group and a methoxy group, both of which were bound to the aromatic ring (2.83 and 4.23 ppm, respectively). On the basis of these results, as well as the results of mixed melting point determination and TLC, compound (I) was identified as 1-acetyl-4-methoxy-β-carboline (I).[2] This is the first report of the isolation of compound (I) from *A. altissima.*

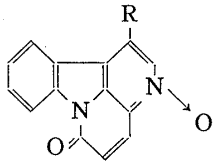
Compound (IIa) was obtained as pale yellow needles with mp 253—254° (dec.). The high resolution mass spectrum of compound (IIa) gave the molecular formula $C_{14}H_{14}N_2O_2$. Since the absorption maxima in the ultraviolet absorption (UV) spectrum (Fig. 1) were very similar to those of 1-ethyl-4-methoxy-β-carboline (IV),[4] it was inferred that compound (IIa) possessed a β-carboline skeleton. In the IR spectrum, absorption bands due to a primary alcohol group were observed at 3240 and 1028 cm^{-1}. The PMR spectrum showed signals



	R	R_1	R_2
	1′ 2′		
I:	$COCH_3$	H	OCH_3
IIa:	CH_2CH_2OH	H	OCH_3
IIIa:	$\underset{\mathrm{OH}}{\mathrm{CH}}\text{-}\mathrm{CH_2OH}$	H	OCH_3
IV:	CH_2CH_3	H	OCH_3
V:	$\underset{\mathrm{OH}}{\mathrm{CH}}\text{-}\mathrm{CH_2OH}$	CH_2OH	H
VI:	CH_2CH_3	H	H
VII:	CH_3	H	H



VIIIa: R=H
VIIIb: R=OCH_3



IXa: R=H
IXb: R=OCH_3

Chart 1

Table I. PMR Spectral Data for Related β-Carbolines[a)]

Compound	3-H	4-H	5-H	6,7,8-H	4-OMe	1′-H	2′-H
I[b)]	8.15 s	—	8.23 d (J=8)	7.30—7.58 m	4.23 s	—	2.83 s
IIa[c)]	7.86 s	—	8.15 d (J=8)	7.23—7.76 m	3.97 s	3.35 t (J=7)	3.66 t (J=7)
IIIa[c)]	7.98 s	—	8.15 d (J=8)	7.12—7.72 m	4.09 s	5.05 t (J=6)	3.18 d (J=6)
IV[b),4)]	8.00 s	—	8.10 d (J=7)	7.10—7.50 m	4.10 s	3.13 q (J=7)	1.40 t (J=7)
VI[b),4)]	8.45 d (J=5)	7.80 d (J=5)	8.10 d (J=7)	7.10—7.57 m	—	3.19 q (J=7)	1.45 t (J=7)

a) Chemical shifts in ppm units; s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. Coupling constants in Hz.
b) In $CDCl_3$ solution.
c) In DMSO-d_6 solution.

due to a methoxy group as a 3H singlet at 3.97 ppm, and two methylene protons, each as a 2H triplet, at 3.35 and 3.66 ppm, which suggested the presence of a hydroxyethyl group. In addition, the ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum showed signals due to a hydroxyethyl group at 28.84 and 63.01 ppm, which suggested a disubstitution of the β-carboline skeleton by comparison with the ^{13}C-NMR spectrum with harman (VII).[5)]

The presence of a hydroxyethyl group and a methoxy group was also supported by the mass spectrum, which showed peaks at *m/e* 224 (M^+-H_2O), 211 (M^+-OCH_3), and 197 ($M^+-CH_2CH_2OH$). To confirm the presence of a hydroxyethyl group, compound (IIa) was acetylated to yield pale yellow needles (IIb, mp 175—177°) which exhibited M^+ at *m/e* 284 in the mass spectrum. The PMR spectrum of IIb showed a signal due to an acetyl group as a 3H singlet at 2.10 ppm, and it was found that a 2H triplet of $C_{2'}$-H in IIa at 3.66 ppm was shifted downfield to 4.48 ppm in IIb. These results indicated the formation of the monoacetate. The above results confirmed the presence of a hydroxyethyl group. In addition, the PMR spectrum of IIa indicated that ring A of the β-carboline was unsubstituted (Table I). The upfield shift of the chemical shift of C_3-H from the normal value of 8.45 ppm to 7.83 ppm indicated methoxy substitution at the C-4 position.[1)]

Compound (IIa), therefore, was identified as 1-(2′-hydroxyethyl)-4-methoxy-β-carboline.

Compound (IIIa) was obtained as pale yellow needles with mp 189—190°. The high resolution mass spectrum of compound (IIIa) gave the molecular formula $C_{14}H_{14}N_2O_3$. As the UV (Fig. 1) and IR spectra of compound (IIIa) were very similar to those of compounds

(IIa) and (IV), it was inferred that compound (IIIa) possessed a β-carboline skeleton carrying hydroxyl and methoxy groups. In the IR spectrum, absorption bands due to hydroxyl, primary alcohol, and secondary alcohol groups were observed at 3320, 1060, and 1150 cm^{-1}, respectively. The PMR spectrum (Table I) showed signals due to a methoxy group as a 3H singlet at 4.09 ppm, methylene protons associated with a primary alcohol group as a 2H doublet at 3.18 ppm and a methine proton associated with a secondary alcohol group as a 1H triplet at 5.05 ppm, which was in good agreement with the chemical shifts of $C_{1'}$–H and $C_{2'}$–H of 1-(1',2'-dihydroxyethyl)-3-hydroxymethyl-β-carboline (V).[6] The C^{13}-NMR spectrum showed signals due to a methoxy group at 56.05 and a 1,2-dihydroxyethyl group at 62.59 and 73.73 ppm, which indicated disubstitution in a β-carboline skeleton in comparison with the ^{13}C-NMR spectra of compounds I, IIa, IIIa, and harman (VII)[5] (Table II). The presence of a 1,2-dihydroxyethyl group and a methoxy group was also supported by the mass spectrum, which showed peaks at m/e 240 (M^+-H_2O), 227 (M^+-OCH_3), and 197 ($M^+-\underset{OH}{C}HCH_2OH$). Compound (IIIa) was then acetylated to yield white needles (IIIb) with mp 140—141°. The mass spectrum of compounds (IIIb) exhibited M^+ at m/e 342, and the PMR spectrum showed signals due to two acetyl groups, each as a 3H singlet, at 2.07 and 2.15 ppm, which was compatible with the formation of a diacetate.

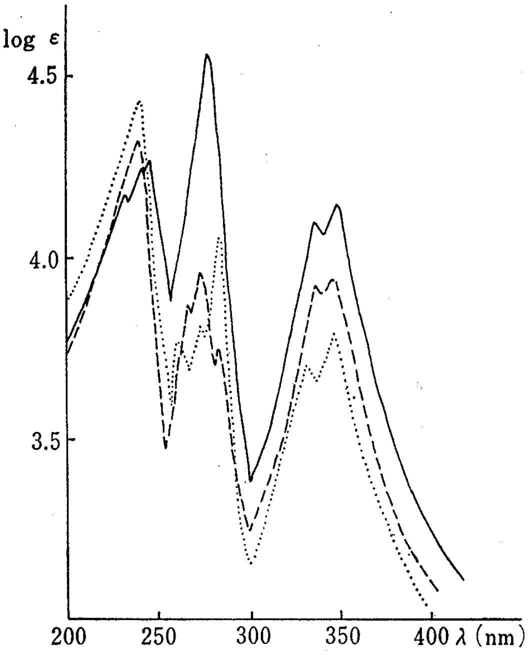


Fig. 1. Ultraviolet Spectra of IIa, IIIa and IV in EtOH

——: IIa, ----: IIIa, ------: IV.

TABLE II. ^{13}C-NMR Spectral Data[a]

Carbon	I[b]	IIa[c]	IIIa[c]	VII[c],[5]
1	139.92 s	137.14 s	139.84 s	141.1 s
3	120.21 d	119.13 d	118.84 d	137.3 d
4	154.56 s	144.56 s	150.59 s	112.4 d
5	124.07 d	121.38 d	123.12 d	121.3 d
6	127.97 d[d]	127.91 d[d]	127.01 d[d]	127.6 d
7	120.89 d[d]	119.28 d[d]	119.35 d[d]	119.1 d
8	111.47 d	112.16 d	111.98 d	111.9 d
10	137.24 s	136.31 s	139.07 s	134.7 s
11	118.55 s	113.62 s	117.26 s	121.2 s
12	121.77 s	119.13 s	119.07 s	127.2 s
13	131.39 s	128.21 s	134.22 s	140.6 s
1'	174.43 s	28.84 t	73.73 d	20.3 q
2'	25.53 q	63.01 t	65.29 t	
OMe	56.42 q	56.03 q	56.05 q	

[a] Chemical shifts in ppm units.
[b] In $CDCl_3$ solution.
[c] In DMSO-d_6 solution.
[d] Assignments may be reversed.

By comparing the PMR (Table I) and UV (Fig. 1) spectra of compound (IIIa) with those of compounds (IIa) and (IV), it was concluded that a methoxy group and 1,2-dihydroxyethyl group were located at C-4 and C-1, respectively.

Compound (IIIa), therefore, was identified as 1-(1′,2′-dihydroxyethyl)-4-methoxy-β-carboline.

Compound (IXb) was obtained as yellow needles with mp 256—257°. The high resolution mass spectrum of compound (IXb) gave the molecular formula $C_{15}H_{10}N_2O_3$. UV absorption maxima were observed at 282, 290, and 374 nm. The IR spectrum showed characteristic bands indicating the presence of an *N*-oxide (1228 cm^{-1}) and a conjugated carbonyl group (1698 and 1650 cm^{-1}). The PMR spectra of VIIIb and IXb were almost identical as regards the chemical shifts of seven protons from C_4–H to C_{10}–H and a 3H singlet of a methoxy group (Table III). Furthermore, 1-methoxycanthin-6-one-3*N*-oxide, obtained by oxidation of VIIIb with *m*-chloroperbenzoic acid, was found to be identical with compound (IXb) by mixed melting point determination and UV, IR, PMR, MS spectra and TLC comparisons.

Table III. PMR Spectral Data for VIIIb and IXb[a)]

Compound	2–H	4–H	5–H	7–H	8–H	9–H	10–H	1–OMe
VIIIb[b)]	8.46 s	6.82 d (J=10)	7.93 d (J=10)	8.64 d (J=8)	7.59 m ($W_{1/2}$=14)	7.42 m ($W_{1/2}$=14)	8.15 d (J=8)	4.25 s
IXb[c)]	8.15 s	6.82 d (J=9)	8.28 d (J=9)	8.60 dd (J=6, 3)	7.48—7.65 m		8.12 dd (J=6, 3)	4.15 s

a) Chemical shifts in ppm units; s=singlet, d=doublet, dd=double doublet, m=multiplet. Coupling constant in Hz.
b) In $CDCl_3$ solution.
c) In $CD_3OD+CDCl_3$ solution.

Compounds VIIIa, VIIIb and IXa were identified by IR, PMR, MS spectra and TLC comparisons and by mixed melting point determinations with authentic canthin-6-one, 1-methoxycanthin-6-one, and canthin-6-one-3*N*-oxide, respectively.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. UV, IR, PMR, ^{13}C-NMR and mass spectra and optical rotation were taken on Hitachi model 340, Hitachi model 295, JEOL model JNM-4H-100, Hitachi model R-900 and JEOL model JMS-01-SG-2 spectrometers, and a JASCO model DIP-4 digital polarimeter, respectively. Column chromatography was performed on silica gel (Wako, C-200). TLC and preparative TLC were carried out on precoated silica gel plates (Merck silica gel 60) and silica gel (Wako, B-5). Development was carried out with $CHCl_3$–MeOH (4: 1) at room temperature, and detection was carried out either by spraying with Dragendorff reagent or by the use of a UV lamp.

Extraction and Fractionation of Alkaloids——Dried chips of the root bark (3.0 kg) of *Ailanthus altissima* Swingle collected in August 1979 at Miyama, Funabashi city, Chiba prefecture, were extracted with methanol under reflux for 48 hr. The extract was concentrated under reduced pressure. The residue was dissolved in water and extracted with $CHCl_3$. The $CHCl_3$ solution was shaken with 5%HCl. The 5%HCl layer was made alkaline to about pH 10 with 5%NH_4OH and extracted with $CHCl_3$. The $CHCl_3$ layer, after being washed with water and dried over Na_2SO_4, was evaporated to dryness under reduced pressure. The crude alkaloids (2.0 g) were applied to a silica gel column, and eluted with benzene, benzene–$CHCl_3$ (19: 1, 9: 1, 5: 1, 2: 1, and 1: 1), $CHCl_3$, $CHCl_3$–MeOH (19: 1, 9: 1, 5: 1, 2: 1, and 1: 1), and MeOH.

1-Acetyl-4-methoxy-β-carboline (I)——The fraction (50 mg) eluted with benzene–$CHCl_3$ (19: 1) was crystallized from benzene, yielding a crystalline compound (I, 6 mg). Pale yellow needles, mp 204—205°. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 238 (4.15), 270 (4.26), 288 (4.23), 370 (3.82). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3350, 1670, 1595, 1338, 1322, 1265, 1190, 1126. PMR and ^{13}C-NMR: The results are shown in Tables I and II. MS *m/e*: 240 (M^+, 100%), 225 (16), 212 (16), 197 (63), 182 (13), 169 (11), 43 (21). High resolution MS, Calcd for $C_{14}H_{12}N_2O_2$: *m/e* 240.0899. Found: *m/e* 240.0867.

1-(2′-Hydroxyethyl)-4-methoxy-β-carboline (IIa)——The fraction (170 mg) eluted with $CHCl_3$–MeOH (19: 1) was subjected to preparative TLC to yield a crystalline compound (IIa, 7 mg). Pale yellow needles, mp 253—254° (dec.). UV λ_{max}^{EtOH} nm (log ε): 232 (4.17), 241 (4.24), 278 (4.53), 336 (4.11), 348 (4.17). IR ν_{max}^{KBr} cm^{-1}: 3240, 1632, 1520, 1320, 1238, 1120, 1028. PMR and ^{13}C-NMR: The results are shown in Tables I and II. MS *m/e*: 242 (M^+, 95%), 227 (70), 224 (100), 212 (64), 197 (61), 169 (45), 44 (22), 43 (15). High resolution MS, Calcd for $C_{14}H_{14}N_2O_2$: *m/e* 242.1055. Found: *m/e* 242.1011.

Acetylation of 1-(2′-Hydroxyethyl)-4-methoxy-β-carboline (IIa)——Compound (IIa, 3 mg) was dissolved in pyridine (0.4 ml) then acetylated with acetic anhydride (0.3 ml). The product was crystallized from acetone to give the monoacetate (IIb, 2 mg), as pale yellow needles, mp 175—177°. PMR ($CDCl_3$) ppm: 2.10 (3H, s, $-OCOCH_3$), 3.39 (2H, t, $J=7$ Hz, $C_1-C\underline{H}_2CH_2OAc$), 4.12 (3H, s, C_4-OCH_3), 4.48 (2H, t, $J=7$ Hz, $C_1-CH_2C\underline{H}_2OAc$), 7.29—7.55 (3H, m, C_6, C_7, C_8–H), 7.83 (1H, s, C_3–H), 8.23 (1H, d, $J=8$ Hz, C_5–H). MS *m/e*: 284 (M^+, 90%), 240 (100), 227 (67), 224 (48), 212 (38), 197 (40), 169 (20), 43 (47).

1-(1′,2′-Dihydroxyethyl)-4-methoxy-β-carboline (IIIa)——The fraction (215 mg) eluted $CHCl_3$–MeOH (19: 1) was subjected to preparative TLC to yield a crystalline substance (63 mg) which was crystallized from $CHCl_3$, yielding a crystalline compound (IIIa, 15 mg). Pale yellow needles, mp 189—190°. $[\alpha]_D^{20}$ $-2.56°$ ($c=0.78$, EtOH). UV λ_{max}^{EtOH} nm (log ε): 240 (4.33), 267 (3.87), 273 (3.97), 286 (3.75), 336 (3.93), 349 (3.95). IR ν_{max}^{KBr} cm^{-1}: 3320, 1560, 1320, 1150, 1060, 835, 780. PMR and ^{13}C-NMR: The results are shown in Table I and II. MS *m/e*: 258 (M^+, 22%), 227 (100), 212 (10), 197 (11), 168 (8). High resolution MS, Calcd for $C_{14}H_{14}N_2O_3$: *m/e* 258.1004. Found: *m/e* 258.1003.

Acetylation of 1-(1′,2′-Dihydroxyethyl)-4-methoxy-β-carboline (IIIa)——Compound (IIIa, 5 mg) was dissolved in pyridine (0.5 ml) then acetylated with acetic anhydride (0.4 ml). The product was crystallized from acetone to give the diacetate (IIb, 5 mg), as white needles, mp 140—141°. IR ν_{max}^{KBr} cm^{-1}: 3280, 1742, 1727, 1595, 1370, 1330, 1250, 1035, 832, 735. PMR ($CDCl_3$) ppm: 2.07 (3H, s, $-OCOCH_3$), 2.15 (3H, s, $-OCOCH_3$), 4.14 (3H, s, C_4-OCH_3), 4.85 (2H, d, $J=5$ Hz, $C_1-\underset{OAc}{\underset{|}{C}}HC\underline{H}_2OAc$), 6.59 (1H, t, $J=5$ Hz, $C_1-\underset{OAc}{\underset{|}{C}}\underline{H}CH_2OAc$), 7.25—7.59 (3H, m, C_6, C_7, C_8–H), 8.03 (1H, s, C_3–H), 8.30 (1H, d, $J=8$ Hz, C_5–H), 9.14 (1H, –NH). MS *m/e*: 342 (M^+), 282 (49), 267 (34), 240 (100), 227 (90), 212 (53), 197 (44).

Canthin-6-one (VIIIa)——The fraction (330 mg) eluted with $CHCl_3$ was crystallized from acetone, yielding a crystalline compound (VIIIa, 250 mg). Pale yellow needles, mp 155—156°. UV λ_{max}^{EtOH} nm (log ε): 259 (4.50), 270 (4.38), 300 (4.29), 362 (4.55), 380 (4.52). IR ν_{max}^{KBr} cm^{-1}: 3037, 1677, 1640, 1609. 1449, 1338, 1321, 1311, 1143, 1056. PMR ($CDCl_3$) ppm: 6.89 (1H, d, $J=10$ Hz, C_4–H), 7.42 (1H, m, $W_{1/2}=17$ Hz, C_9–H), 7.61 (1H, m, $W_{1/2}=17$ Hz, C_8–H), 7.82 (1H, d, $J=5.5$ Hz, C_1–H), 7.92 (1H, d, $J=10$ Hz, C_5–H), 7.97 (1H, q, $J=8$ Hz, C_{10}–H), 8.54 (1H, q, $J=8$ Hz, C_7–H), 8.73 (1H, d, $J=5.5$ Hz, C_2–H). MS *m/e*: 220 (M^+, 100%), 192 (70), 164 (25), 139 (22), 114 (15), 96 (18).

1-Methoxycanthin-6-one (VIIIb)——The fraction (170 mg) eluted with $CHCl_3$–MeOH (19:1) was crystallized from acetone, yielding a crystalline compound (VIIIb, 75 mg). Pale yellow needles, mp 250—250.5°. UV λ_{max}^{EtOH} nm (log ε): 279.5 (4.09), 330 (3.87), 361.5 (4.24), 370 (4.21), 378.5 (4.28). IR ν_{max}^{KBr} cm^{-1}: 3047, 1685, 1635, 1609, 1486, 1331, 1262. PMR: The results are shown in Table III. MS *m/e*: 250 (M^+ 100%), 235 (22), 207 (56), 179 (26), 149 (43), 125 (28).

Canthin-6-one-3*N*-oxide (IXa)——The fraction (70 mg) eluted with $CHCl_3$–MeOH (19: 1) was crystallized from MeOH, yielding a crystalline compound (IXa, 35 mg). Pale yellow needles, mp 244—245° (dec.). UV λ_{max}^{KBr} nm (log ε): 246.5 (4.07), 279.5 (4.38), 370 (4.13). IR ν_{max}^{KBr} cm^{-1}: 3057, 1677, 1644, 1428, 1326, 1230, 1063. PMR ($CDCl_3$) ppm: 6.92 (1H, d, $J=11$ Hz, C_4–H), 7.42—7.72 (2H, m, C_8, C_9–H), 7.78 (1H, d, $J=6$ Hz, C_1–H), 7.96 (1H, m, $W_{1/2}=12$ Hz, C_{10}–H), 8.32 (1H, d, $J=6$ Hz, C_2–H), 8.37 (1H, d, $J=11$ Hz, C_5–H), 8.61 (1H, m, $W_{1/2}=12$ Hz, C_7–H). MS *m/e*: 236 (M^+, 100%), 220 (43), 208 (21), 192 (40), 191 (24), 179 (27), 164 (25), 149 (37).

1-Methoxycanthin-6-one-3*N*-oxide (IXb)——The fraction (220 mg) eluted with $CHCl_3$-MeOH (19: 1) was subjected to preparative TLC to yield a crystalline substance (20 mg), which was crystallized from $CHCl_3$, yielding a crystalline compounds (IXb, 13 mg). Yellow needles, mp 256—257°. UV λ_{max}^{EtOH} nm (log ε): 282 (4.04), 290 (4.19), 374 (3.95). IR ν_{max}^{KBr} cm^{-1}: 3060, 1698, 1650, 1590, 1372, 1228, 1078, 986, 830. PMR: The results are shown in Table III. MS *m/e*: 266 (M^+, 100%), 250 (25), 235 (4), 223 (29), 207 (18), 179 (24), 168 (9). The high resolution MS, Calcd for $C_{15}H_{10}N_2O_3$: *m/e* 266.0691. Found: *m/e* 266.0664.

Conversion of 1-Methoxycanthin-6-one (VIIIb) to 1-Methoxycanthin-6-one-3*N*-oxide (IXb)——A solution of VIIIb (26 mg) in $CHCl_3$ (2 ml) was added to *m*-chloroperbenzoic acid (20 mg) in $CHCl_3$ (1 ml). After 17 hr, the reaction mixture was washed with 5%$NaHCO_3$ and H_2O. The $CHCl_3$ layer was dried over Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was crystallized from $CHCl_3$ to give IXb (19 mg) as yellow needles, mp 256—257°. The spectral data were identical with those of an authentic sample of the natural product, and the mixed mp was undepressed.

Acknowledgement The authors are very grateful to Dr. B.S. Joshi (CIBA-GEIGY Research Center) for his generous gift of authentic 1-acetyl-4-methoxy-β-carboline. Thanks are due to Mr M. Takayama of this school for mass spectra and to Miss M. Suganuma (Nissan Chem. Ind. Co.) for NMR spectra.

References and Notes

1) Part I: T. Ohmoto, R. Tanaka, and T. Nikaido, *Chem. Pharm. Bull.*, **24**, 1532 (1976).
2) B.S. Joshi, V.N. Kamat, and D.H. Gawad, *Heterocycles*, 7, 193 (1977).
3) A part of this work was presented at the Annual Meeting of the Pharmacognostical Society of Japan, Chiba, October, 1975.
4) E. Sánchez and J. Comin, *Phytochemistry*, **10**, 2155 (1971).
5) H. Wagnar and T. Nestler, *Tetrahedron Lett.*, **31**, 277 (1978).
6) M. Kumagai, H. Naganawa, T. Aoyagi, and H. Umesawa, *J. Antibiot.* (Tokyo), Ser. A., **28**, 876 (1975).