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Chemical Constituents of *Murraya euchrestifolia* HAYATA. Structures of Novel Carbazolequinones and Other New Carbazole Alkaloids

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Thirteen carbazole alkaloids were isolated from *Murraya euchrestifolia* HAYATA (Rutaceae) collected in Taiwan. Four of them are novel carbazolequinones [murrayaquinone-A (**7**), -B (**8**), -C (**9**), and -D (**10**)], isolated for the first time from natural sources. Three of others are new alkaloids having the normal carbazole nucleus [murrayafoline-A (**1**), -B (**2**), and (+)-murrayazoline (**11**)]. These structures were elucidated from spectral data and chemical transformations.

Keywords——murrayaquinone; murrayafoline; murrayazoline; *Murraya euchrestifolia*; Rutaceae; carbazole alkaloid; carbazolequinone; Fremy's salt

Introduction

The plants of the genus *Murraya*, growing naturally in Southern Asia, are shrubs belonging to Rutaceae.[1] Extracts of the leaves and bark of this tree have been used as a folk medicine for analgesia and local anesthesia, and for the treatment of eczema, rheumatism, and dropsy. The plants of this genus are also known as a major source of carbazole alkaloids.[2,3] We report here that systematic fractionation of the constituents of the root bark of *Murraya euchrestifolia* HAYATA gave three new carbazole alkaloids, murrayafoline-A (**1**) and -B (**2**), and (+)-murrayazoline (**11**), and four novel carbazolequinone alkaloids, murrayaquinone-A (**7**), -B (**8**), -C (**9**), and -D (**10**), as well as six known carbazoles, *p*-hydroquinone, and *p*-hydroxybenzoic acid.

This is the first report of the isolation of carbazolequinone alkaloids from a natural source.[4]

Results and Discussion

The ethanolic extract of root bark of *Murraya euchrestifolia* HAYATA was treated in the manner described in the experimental section, and each compound was isolated.

Structure of Murrayafoline-A (1)

Murrayafoline-A was obtained as colorless plates, mp 52—53 °C; its picrate as brown needles, mp 188—190 °C. The base showed a yellow color in conc. sulfuric acid. The ultraviolet (UV) absorption bands at λ_{max} 225, 243, 251 sh, 283 sh, 292, 330, and 344 sh nm were similar to those of 1-oxygenated carbazoles.[3] The infrared (IR) absorption band at ν_{max} 3480 cm^{-1} and proton nuclear magnetic resonance (^{1}H-NMR) peak at δ 7.96 (slowly exchanged on deuteration) together with a negative color reaction to alcoholic iron (III) chloride, indicated the presence of an imino group rather than a phenolic hydroxy group. In

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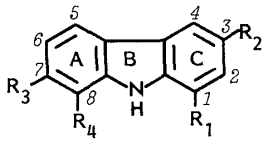
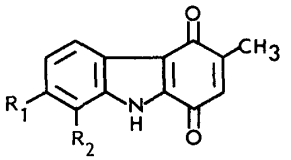
the ^{1}H-NMR spectrum of murrayafoline-A, a lower doublet signal at δ 7.87 (J=8 Hz) is characteristic of 5-H on the carbazole.[3] The overlapped three-proton signals at δ 6.9—7.3 along with the 5-H signal at δ 7.87 suggested a lack of substituents on ring A. Two further singlets in the aromatic proton region were observed at δ 6.55 and 7.33. Two three-proton singlets at δ 3.76 and 2.42 were assigned to a methoxy and an aryl methyl group, respectively. In a nuclear Overhauser effect (NOE) experiment, irradiation of the methoxy signal at δ 3.76 caused an 18.5% enhancement of the signal at δ 6.55 (2-H). As expected, irradiation of the aryl methyl signal at δ 2.42 caused a 9.6% and 9.5% enhancements of the aromatic proton signals at δ 7.33 (4-H) and 6.55 (2-H), respectively.

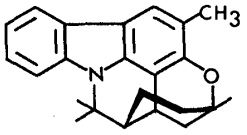
These spectral data suggested the structure of murrayafoline-A to be formula **1**. A synthesis of this compound has been reported by Chakraborty and Chowdhury.[5] However, this is the first reported occurrence in a natural source.



	R_1	R_2	R_3	R_4
1	OCH_3	CH_3	H	H
2	OH	CH_3	OCH_3	prenyl
3	OCH_3	CHO	H	H
4	H	CH_3	H	H
5	OCH_3	COOH	H	H
6	OH	CH_3	H	H



	R_1	R_2
7	H	H
8	OCH_3	prenyl
9	OCH_3	geranyl
10	OH	geranyl



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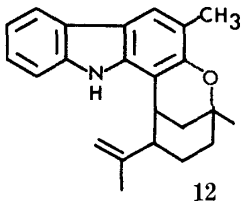

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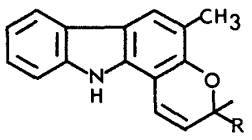

	R
13	CH_3
14	$CH_2CH_2CH{=}C(CH_3)_2$

Chart 1

Structure of Murrayafoline-B (2)

Murrayafoline-B was isolated as a colorless syrup. The UV spectrum showed typical absorption associated with a carbazole nucleus[2,3] (see the experimental section), and a bathochromic shift was observed on addition of sodium hydroxide, indicating the presence of a phenolic hydroxy group. The ^{1}H-NMR spectrum showed the presence of a prenyl [δ 1.72 (3H, s), 1.88 (3H, s), 3.60 (2H, d, J=8 Hz), and 5.30 (1H, t, J=8 Hz)] and a methoxy group [δ 3.90 (3H, s)]. Of the AB-type signals at δ 7.72 and 6.82 (each 1H, d, J=9 Hz), the lower field signal at δ 7.72 is well known as being characteristic of 5-H of carbazoles, thus suggesting the location of substituents at 7-C and 8-C. The remaining two one-proton singlets at δ 6.56 and 7.32 in the aromatic proton region were assigned to 2-H and 4-H, respectively, being consistent with those in the ^{1}H-NMR spectrum of **1**. Two one-proton singlets at δ 4.99 and 7.94, which disappeared on addition of deuterium oxide, were assigned to a hydroxy and an imino proton, respectively.

Photooxidation of murrayafoline-B in methanol gave deep purplish needles, mp 221—223 °C, which were shown to be identical with murrayaquinone-B (**8**) described below, by IR, ^{1}H-NMR, and thin layer chromatography (TLC) comparisons, and mixed melting point

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determination.

Consequently, murrayafoline-B may be represented by structure **2**.

Structure of Murrayaquinone-A (7)

Murrayaquinone-A was isolated as brown prisms, mp 246—247 °C. This alkaloid showed the molecular ion peak at *m/z* 211 in the mass spectrum (MS), and microanalysis established the molecular formula as $C_{13}H_9NO_2$. The presence of a carbazole-1,4-quinone nucleus in the molecule was suggested by the UV absorption bands at λ_{max} 225, 258, 293 sh, and 398 nm and IR bands at ν_{max} 3200, 1650, and 1595 cm^{-1},[6,7] coupled with the appearance of two carbonyl carbon signals at δ 183.4 and 180.4 in the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum. In the ^{1}H-NMR spectrum, a three-proton multiplet in the region at δ 7.30—7.60 could be assigned to ring A protons (6-, 7-, and 8-H), and a one-proton double triplet centered at δ 8.23 (J = 1 and 5 Hz) was attributable to 5-H which was affected by deshielding due to the carbonyl moiety at 4-C. In addition, an allyl methyl signal at δ 2.19 (3H, d, J = 1.5 Hz) and an olefinic proton at δ 6.51 (1H, q, J = 1.5 Hz), both having a long range coupling, were observed. The presence of a methyl group at 3-C (not at 2-C) of the carbazolequinone nucleus was suggested by biogenetic considerations[2,3] and by the appearance of an olefinic proton signal at δ 6.51 (if an olefinic proton were located at 3-C, a somewhat more downfield shift would be expected[8]).

Photooxidation of murrayafoline-A (**1**) or oxidation of 1-hydroxy-3-methylcarbazole (**6**)[5] with Fremy's salt afforded the same brown prisms, mp 246—247 °C as a sole product, which was shown to be identical with murrayaquinone-A obtained from the natural source by IR, ^{1}H-NMR and mass spectral comparisons and mixed melting point determination.

These results led us to assign structure **7** to murrayaquinone-A.

Structure of Murrayaquinone-B (8)

Murrayaquinone-B was obtained as deep purplish needles, mp 221—223 °C. The high resolution MS gave the molecular formula $C_{19}H_{19}NO_3$. The UV and ^{13}C-NMR spectra suggested that murrayaquinone-B possessed a carbazole-1,4-quinone skeleton, the same as that of **7**. In the ^{1}H-NMR spectrum, AB-type proton signals at δ 7.02 (d, J = 9 Hz) and 7.98 (d, J = 9 Hz) were attributed to mutually *ortho*-located protons on the aromatic ring, and the lower field signal could be assigned to 5-H. The presence of a methoxy, an allyl methyl and a prenyl group in the molecule was confirmed by NMR and/or MS. The appearance of a 15.2% enhancement of the signal at δ 6.42 on irradiation of the methyl proton (δ 2.13) in an NOE experiment, and the chemical shift value of 2-C (δ 131.5) in the ^{13}C-NMR spectrum of murrayaquinone-B, closely related to that of murrayaquinone-A (**7**) (δ 131.6), suggested the same partial structure of ring C as in **7**. Further, the observation of a 15.9% NOE enhancement between 6-H at δ 7.02 and the methoxy signal at δ 3.91 was suggestive of the location of a methoxy and a prenyl group at 7-C and 8-C, respectively.

On the basis of these spectral data, the structure of murrayaquinone-B should be represented by formula **8**.

Structure of Murrayaquinone-C (9), and -D (10)

Murrayaquinone-C, mp 158—159 °C, and murrayaquinone-D, mp 164—168 °C, have the molecular formulae $C_{24}H_{27}NO_3$ (M^+, *m/z* 377) and $C_{23}H_{25}NO_3$ (M^+, *m/z* 363), respectively, and their UV absorptions suggested that they possessed the same carbazole-1,4-quinone structure.[6-8] This was also supported by the appearance of two carbonyl carbon signals at δ 183.6 and 179.7 in the ^{13}C-NMR spectrum of murrayaquinone-C. The ^{1}H-NMR spectra (Table I) of these alkaloids showed similar signal patterns, except for an additional methoxy signal in that of murrayaquinone-C. Treatment of murrayaquinone-D with diazomethane gave a mono-*O*-methyl ether, which was identical with murrayaquinone-C. The

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presence of a geranyl group in murrayaquinone-C was indicated by the ^{1}H-NMR spectrum [δ 1.56 (3H, s), 1.61 (3H, s), 1.85 (3H, s), 2.05 (4H, s), 3.58 (2H, d, J=7 Hz), 5.03 (1H, m), and 5.26 (1H, t, J=7 Hz)] and the ^{13}C-NMR spectrum [δ 131.6 (s), 123.9 (d), 121.5 (d), 39.6 (t), 26.6 (t), 25.6 (q), 23.7 (t), 17.7 (q), and 16.4 (q)], together with mass fragments at m/z 308 [$M^+ - \cdot CH_2CH=C(CH_3)_2$] and 254 [$M^+ - \cdot CH_2CH=C(CH_3)-CH_2CH=C(CH_3)_2$]. Other signals closely resembled those of murrayaquinone-B (**8**) (Table I). An NOE experiment on murrayaquinone-C showed that the signal at δ 7.01, one of the *ortho* coupled protons, showed a 14.9% enhancement on irradiation of the methoxy signal at δ 3.91. Irradiation of the allyl methyl signal at δ 2.13 gave a 16.9% enhancement of the olefinic proton signal at δ 6.41.

These data led us to the structures **9** and **10** for murrayaquinone-C and -D, respectively.

Further, colorless needles, mp 276—278 °C, $[\alpha]_D$ +2.25° (in chloroform) were obtained from the same plant. This product was assigned the molecular formula $C_{23}H_{25}NO$ by elemental analysis, and the physical and spectral (IR, UV, ^{1}H-NMR, and MS) properties of this alkaloid were in agreement with those of (−)-murrayazoline (enantiomer of **11**),[9] except for the optical rotation. Racemic murrayazoline, named mahanimbidine[10] and curryangin,[11] has been isolated from *Murraya koenigii* SPRENG. However, this is the first example of isolation of murrayazoline having a positive optical rotation.

Other constituents isolated from the same plant material were characterized as murrayanine (**3**),[5,12] girinimbine (**13**),[13] mahanimbine (**14**),[14] *p*-hydroxybenzoic acid, *p*-hydroquinone, and β-sitosterol by comparison with authentic samples (^{1}H-NMR, IR and MS and/or mixed melting point determination). The physical constants and spectroscopic data (UV, IR, and ^{1}H-NMR) of **4**, **5**, and **12** were in agreement with those described in the literature for 3-methylcarbazole,[15] mukoeic acid[16] and cyclomahanimbine.[17] Further studies of other compounds (A, B, C, and ME-1—6) described in the experimental section are in progress.

The carbazolequinones were found in the root bark of *Murraya euchrestifolia* collected in August and December. However, these alkaloids could not be detected in the plant collected in February in the same district. The seasonal variation of the constituents of this plant is very

TABLE I. ^{1}H-NMR Spectral Data for New Carbazole Alkaloids from *Murraya euchrestifolia*

	1	**2**	**7**	**8**	**9**	**10**	**11**
2-H	6.55 (s)	6.56 (s)	6.51 (q, 1.5)	6.42 (q, 1.5)	6.41 (q, 2)	6.41 (q, 2)	
4-H	7.33 (s)	7.32 (s)					7.44 (s)
5-H	7.87 (d, 8)	7.72 (d, 9)	8.23 (dt, 1, 5)	7.98 (d, 9)	7.98 (d, 9)	7.88 (d, 9)	7.86 (dd, 3, 7)
6-H	6.90	6.82 (d, 9)	7.30	7.02 (d, 9)	7.01 (d, 9)	6.86 (d, 9)	7.00
7-H	≀ (3H, m)		≀ (3H, m)				≀ (3H, m)
8-H	7.30		7.60				7.50
Ar-CH_3	2.40 (s)	2.42 (s)	2.19 (d, 1.5)	2.13 (d, 1.5)	2.13 (d, 2)	2.12 (d, 2)	2.30 (s)
OCH_3	3.76 (s)	3.90 (s)		3.91 (s)	3.91 (s)		
NH	7.98 (br s)	7.94 (s)	9.20 (br s)	9.07 (br s)	9.08 (s)	9.07 (br s)	
OH		4.99 (s)				5.52 (s)	
1′-H		3.60 (d, 8)		3.57 (d, 7)	3.58 (d, 7)	3.51 (d, 7)	
2′-H		5.30 (t, 8)		5.23 (br t, 7)	5.26 (t, 7)	5.32 (t, 7)	
3′-H							3.25 (1H, m)
5′,6′-H					2.05 (4H, s)	2.07 (4H, s)	
7′-H					5.07 (1H, m)	5.04 (1H, m)	
CH_3		1.72 (3H, s)		1.74 (3H, s)	1.56 (3H, s)	1.58 (3H, s)	1.26 (3H, s)
		1.88 (3H, s)		1.85 (3H, s)	1.61 (3H, s)	1.64 (3H, s)	1.43 (3H, s)
					1.85 (3H, s)	1.85 (3H, s)	1.87 (3H, s)

Taken in $CDCl_3$. Values are in ppm. Multiplicities are indicated by the usual symbols: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, double doublet; dt, doublet triplet; br, broad. Figures in parentheses are coupling constants in Hz.

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interesting from the biogenetic viewpoint.

Experimental

All melting points were measured on a micromelting point hot-stage apparatus (Yanagimoto). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on PS-100 (JEOL) and FX-100 (JEOL) spectrometers, respectively in $CDCl_3$, unless otherwise stated. Chemical shifts are shown in δ-values (ppm) with tetramethylsilane (TMS) as internal reference. MS were taken with an M-52 (Hitachi) spectrometer having a direct inlet system, and high resolution mass spectra with an M-80 (Hitachi) spectrometer. UV spectra were determined in methanol and IR spectra were recorded in KBr disc, unless otherwise stated.

Extraction and Separation——a) The dried root bark (2.7 kg) of *Murraya euchrestifolia* HAYATA collected at Kuantaochi, Nantou Hsien, Taiwan, in February, 1980, was chipped and extracted with ethanol under reflux. The ethanolic extract was partitioned between chloroform and water. The chloroform layer was separated, dried and concentrated to give a brown syrup. This was subjected to silica gel column chromatography with successive elution with hexane, benzene, and benzene–acetone (9 : 1). The hexane eluate was concentrated to give a thick syrup. Picric acid was added to a benzene solution of this syrup, and the precipitate was filtered off. The filtrate was concentrated, made alkaline with diluted aqueous ammonia and extracted with chloroform. The chloroform layer was dried over anhydrous sodium sulfate, taken to dryness *in vacuo* and then subjected to silica gel column chromatography with hexane–isopropyl ether (4 : 1) to afford (+)-murrayazoline (**11**) (56 mg), mahanimbine (**14**) (140 mg), cyclomahanimbine (**12**) (1.1 g), girinimbine (**13**) (23 mg), β-sitosterol (500 mg), ME-2 (70 mg), ME-4 (18 mg), and 3-methylcarbazole (**4**) (21 mg) successively.

The benzene eluate was rechromatographed on silica gel and developed with hexane–ethyl acetate (4 : 1) to afford ME-1 (67 mg), ME-3 (3 mg), ME-6 (6 mg), compound A (10 mg), and murrayanine (**3**) (910 mg) successively. Mukoeic acid (**5**) (35 mg) and *p*-hydroxybenzoic acid (15 mg) were obtained from the benzene–acetone (9 : 1) eluate.

The precipitate of picrate was treated with diluted aqueous ammonia and extracted with chloroform. The chloroform layer was dried and concentrated to give murrayafoline-A (**1**) (31 g).

b) The dried powdered root bark (900 g) of *M. euchrestifolia* collected at the same district in December 1982, was extracted with acetone. The acetone extract was concentrated to give a brown syrup, which was chromatographed on silica gel with hexane, benzene and benzene–acetone (9 : 1) successively as eluents. The hexane eluate was rechromatographed on silica gel with hexane–isopropyl ether (4 : 1) to afford murrayafoline-A (**1**) (5.5 g), (+)-murrayazoline (**11**) (50 mg) and mahanimbine (**14**) (80 mg) successively. The benzene eluate was also subjected to silica gel column chromatography with hexane–ethyl acetate (4 : 1) to give girinimbine (**13**) (800 mg), β-sitosterol (200 mg), murrayaquinone-B (**8**) (95 mg), -C (**9**) (15 mg), -D (**10**) (5 mg), -A (**7**) (3 mg), compound B (2 mg), compound C (3 mg), murrayafoline-B (**2**) (6 mg), ME-2 (30 mg), ME-5 (6 mg), ME- 4 (20 mg), and murrayanine (**3**) (1.1 g) successively. The benzene–acetone (9 : 1) eluate gave *p*-hydroquinone (40 mg).

Murrayafoline-A (1)——Colorless plates, mp 52—54 °C (from hexane). Picrate: brown needles, mp 188—190 °C (from benzene). UV λ_{max} nm (log ε): 225 (4.47), 243 (4.58), 251 sh (4.44), 283 sh (3.83), 292 (4.01), 330 (3.53), 344 inf (3.49). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3480, 1640, 1610, 1590, 1505. MS *m/z* (%): 211 (M^+, 100), 196 (89), 180 (10), 168 (54), 167 (33). ^{13}C-NMR δ: 145.2 (s), 139.5 (s), 129.2 (s), 128.0 (s), 125.4 (d), 124.3 (s), 123.4 (s), 120.3 (d), 119.1 (d), 112. 5(d), 110.9 (d), 107.7 (d), 55.1 (q), 21.8 (q).

Murrayafoline-B (2)——Colorless syrup. UV λ_{max} nm: 230 sh, 247, 255 sh, 302, 324 sh, and 337 sh. UV λ_{max}^{NaOH} nm: 234, 254, 304, 338 nm. IR ν_{max} cm^{-1}: 3600, 3475, 1620, 1595. MS *m/z*: 295 (M^+, 100%), 280, 264, 252, 240 ($M^+ - 55$), 227 ($M^+ - 68$), 210.

Murrayanine (3)——Colorless plates, mp 168—169 °C (from chloroform). UV λ_{max} nm (log ε): 208 sh (4.18), 222 sh (4.27), 238 (4.45), 247 sh (4.30), 273 (4.53), 287 (4.35), 330 (4.15), 340 (4.15). IR ν_{max} cm^{-1}: 3150, 1650, 1615, 1600, 1575. MS *m/z*: 225 (M^+, 100%), 210, 196, 182, 168, 167, 166, 154, 139. ^{1}H-NMR (acetone-d_6) δ: 4.02 (3H, s, OCH_3), 7.16 (1H, dt, J=2, 8 Hz, 6-H), 7.33 (1H, s, 2-H), 7.34 (1H, dt, J=2, 8 Hz, 7-H), 7.55 (1H, dd, J=2, 8 Hz, 8-H), 8.08 (1H, dd, J=2, 8 Hz, 5-H), 8.20 (1H, s, 4-H), 9.92 (1H, s, CHO), 10.87 (1H, br s, NH).

3-Methylcarbazole (4)——Colorless prisms, mp 206—207 °C (from acetone). UV λ_{max} nm: 216 sh, 230 sh, 236, 246 sh, 260, 290 sh, 296, 328, 342. IR ν_{max} cm^{-1}: 3380, 1600, 1490, 1450. MS *m/z*: 181 (M^+, 100%), 180, 152. ^{1}H-NMR (acetone-d_6) δ: 2.45 (3H, s, aryl CH_3), 6.96—7.50 (5H, m, 1-, 2-, 6-, 7-, 8-H), 7.82 (1H, s, 4-H), 7.99 (1H, d, J=8 Hz, 5-H), 10.10 (1H, br s, NH).

Mukoeic Acid (5)——Colorless needles, mp 243—245 °C (from acetone). UV λ_{max} nm: 236, 244 sh, 268 sh, 276, 310, 320, 333 sh. IR ν_{max} cm^{-1}: 3395, 1665, 1630, 1600, 1580. MS *m/z*: 241 (M^+, 100%), 226, 211, 198. ^{1}H-NMR (acetone-d_6) δ: 4.07 (3H, s, OCH_3), 7.10—7.65 (4H, m, 6-, 7-, 8-H, and COOH), 7.56 (1H, s, 2-H), 8.15 (1H, d, J= 8 Hz, 5-H), 8.47 (1H, s, 4-H), 10.71 (1H, br s, NH).

Murrayaquinone-A (7)——Brown prisms, mp 246—247 °C (from acetone). *Anal.* Calcd for $C_{13}H_9NO_2$: C, 73.92; H, 4.30; N, 6.63. Found: C, 73.46; H, 4.14; N, 6.30. UV λ_{max} nm (log ε): 225 (4.63), 258 (4.51), 293 sh (3.85), 398 (3.93). IR ν_{max} cm^{-1}: 3200, 1650, 1595. MS *m/z*: 221 (M^+, 100%), 196, 183, 168, 81, 69. ^{13}C-NMR ($CDCl_3$ + DMSO-d_6) δ:

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183.4 (s), 180.4 (s), 148.3 (s), 137.8 (s), 136.0 (s), 131.6 (d), 126.1 (d), 124.1 (s), 123.7 (d), 122.2 (d), 116.2 (s), 113.7 (d), 16.0 (q).

Murrayaquinone-B (8)——Deep purplish needles, mp 221—223 °C (from acetone). High resolution MS Calcd for $C_{19}H_{19}NO_3$: 309.1363. Found: 309.1360. UV λ_{max} nm (log ε): 210 sh (4.28), 231 (4.58), 264 (4.44), 310 sh (3.21), 404 (3.66). IR ν_{max} cm^{-1}: 3280, 1655, 1640, 1610. MS *m/z* (%): 309 (M^+, 100), 294 (42), 279 (33), 278 (21), 266 (14), 264 (14), 254 (62), 241 (17), 154 (23), 81 (14), 69 (29). ^{13}C-NMR δ: 183.7 (s), 179.8 (s), 156.0 (s), 148.2 (s), 138.0 (s), 135.1 (s), 133.9 (s), 131.5 (d), 121.6 (d), 121.1 (d), 119.1 (s), 117.2 (s), 112.7 (s), 110.8 (d), 56.7 (q), 25.7 (q), 23.7 (t), 18.0 (q), 16.1 (q).

Murrayaquinone-C (9)——Violet needles, mp 158—159 °C (from ether). UV λ_{max} nm: 233, 267, 410. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3440, 1655, 1645, 1620, 1610. MS *m/z*: 377 (M^+, 100%), 308 (M^+-69), 293, 278, 255, 254 (M^+-123), 240, 224; ^{13}C-NMR δ: 183.6 (s), 179.7 (s), 156.0 (s), 148.1 (s), 138.0 (s), 137.5 (s), 135.1 (s), 131.6 (s), 131.5 (d), 123.9 (d), 121.5 (d), 121.1 (d), 119.1 (s), 117.2 (s), 112.7 (s), 110.8 (d), 56.7 (q), 39.6 (t), 26.6 (t), 25.6 (q), 23.7 (t), 17.7 (q), 16.4 (q), 16.0 (q).

Murrayaquinone-D (10)——Violet needles, mp 164—168 °C. UV λ_{max} nm: 215 sh, 234, 266, 415. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3440, 3300, 1660, 1645, 1620, 1610, 1545, 1520. MS *m/z*: 363 (M^+, 100%), 313 (M^+-50), 294 (M^+-69), 280, 279, 278, 266, 262, 252, 241, 240 (M^+-123), and 227.

(+)-Murrayazoline (11)——Colorless needles, mp 276—278 °C (from acetone), $[\alpha]_D^{25}$ +2.25° (*c*=0.4, $CHCl_3$). High resolution MS Calcd for $C_{23}H_{25}NO$: 331.1935. Found: 331.1949. UV λ_{max} nm (log ε): 223 sh (4.39), 246 (4.66), 261 sh (4.29), 309 (4.14), 341 (3.66). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1635, 1600, 1480, 1450. MS *m/z* (%): 331 (M^+, 100), 315 (54), 301 (5), 288 (10), 248 (63), 210 (11).

Cyclomahanimbine (12)——Colorless prisms, mp 138—139 °C (from ether), $[\alpha]_D^{25}$ +0° (*c*=0.8, $CHCl_3$). Picrate: deep blue needles, mp 166—168 °C (from ether). UV λ_{max} nm: 217, 241, 255, 306, 332 sh. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3440, 1625, 1615, 1575. MS *m/z*: 331 (M^+), 316, 288, 262, 248 (100%), 210. ^{1}H-NMR δ: 1.42, 1.49 (each 3H, s, CH_3), 1.50—2.10 (6H, m, 3 CH_2), 2.31 (3H, s, aryl CH_3), 2.50 (1H, m, allyl CH), 3.34 (1H, q, *J*=3 Hz, benzylic H), 4.74 (2H, m, vinylic CH_2), 7.04—7.40 (3H, m, 6-, 7-, 8-H), 7.63 (1H, s, 4-H), 7.70 (1H, br s, NH), 7.89 (1H, d, *J*=7 Hz, 5-H).

Girinimbine (13)——Colorless plates, mp 177—178 °C (from acetone). *Anal.* Calcd for $C_{18}H_{17}NO$: C, 82.03; H, 6.57; N, 5.14. Found: C, 81.93; H, 6.62; N, 5.13. UV λ_{max} nm: 223, 236, 278 sh, 287, 314 sh, 328, 343, 358. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3470, 1640, 1610. MS *m/z*: 263 (M^+), 248 (100%), 218, 204, 131, 124. ^{1}H-NMR (acetone-d_6) δ: 1.47 (6H, s, 2×CH_3), 2.26 (3H, s, aryl CH_3), 5.72, 6.86 (each 1H, d, *J*=10 Hz, olefinic H), 6.95—7.40 (3H, m, 6-, 7-, 8-H), 7.65 (1H, s, 4-H), 7.88 (1H, d, *J*=8 Hz, 5-H), 10.18 (1H, br s, NH).

***dl*-Mahanimbine (14)**——Colorless needles, mp 92—94 °C (from hexane), $[\alpha]_D^{25}$ +0° (*c*=0.4, $CHCl_3$). UV λ_{max} nm: 223 sh, 239, 280 sh, 288, 318 sh, 330, 343, 359 nm. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3470, 1640, 1605. MS *m/z*: 331 (M^+), 316 (100%), 288, 262, 248, 204. ^{1}H-NMR δ: 1.43, 1.56, 1.64 (each 3H, s, CH_3), 2.29 (3H, s, aryl CH_3), 5.04 (1H, m, vinylic H), 5.55, 6.50 (each 1H, d, *J*=10 Hz, olefinic H), 6.96—7.30 (3H, m, 6-, 7-, 8-H), 7.53 (1H, s, 4-H), 7.68 (1H, s, NH) 7.79 (1H, d, *J*=7 Hz, 5-H).

Oxidation of 1-Hydroxy-3-methylcarbazole (6) with Fremy's Salt——A solution of 1-hydroxy-3-methylcarbazole (**6**)[5] (90 mg) in acetone (20 ml) was slowly added to a mixture of potassium nitrosodisulfonate (350 mg) and KH_2PO_4 (20 mg) in H_2O (20 ml). The mixture was stirred at room temperature for 30 min, and then evaporated to remove acetone. The precipitate was filtered off and washed with H_2O, and the filtrate and washings were evaporated to dryness. The residue was crystallized from acetone to give brown prisms (83 mg), mp 246—247 °C, which were shown to be identical with murrayaquinone-A (**7**) by comparison of the IR and MS, and mixed melting point determination.

Photooxidation of Murrayafoline-A (1)——A solution of murrayafoline-A (**1**) (50 mg) in methanol (50 ml) was irradiated with a high pressure 500W Hg lamp for 30 min, and then the reaction mixture was evaporated to dryness. Column chromatography of the residue on silica gel with hexane–ethyl acetate (4 : 1) as the eluent gave brown prisms (5 mg), mp 245—247 °C, which were recrystallized from acetone. This product was shown to be identical (IR, MS, and mixed melting point test) with murrayaquinone-A (**7**).

Photooxidation of Murrayafoline-B (2)——Murrayafoline-B (**2**) (5 mg) was treated as described for the photoxidation of **1** to afford deep purplish needles (4 mg), mp 220—222 °C. This product was shown to be identical (IR, NMR, and mixed melting point test) with murrayaquinone-B (**8**).

Methylation of Murrayaquinone-D (10)——An excess of ethereal diazomethane was added to methanol solution of murrayaquinone-D (3 mg) and mixture was kept at room temperature overnight. The solvent was removed and the residue was crystallized from ether to give violet needles, mp 157—159 °C (3 mg), which were shown to be identical (IR, NMR, MS, and mixed melting point test) with murrayaquinone-C (**9**).

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References

1) C.-E. Chang, "Flora of Taiwan," Vol. 3, Epoch Publishing Co., Ltd., Taipei, Taiwan, 1977, pp. 520—523.
2) R. S. Kapil, "The Alkaloids," Vol. 13, ed. by R. H. F. Manske, Academic Pr., New York, 1971, Chapter 6.
3) D. P. Chakraborty, "Fortschritte d. Chem. Org. Naturst.," Vol. 34, ed. by W. Herz, H. Grisebach, and G. W. Kirby, Springer–Verlag, New York, 1977, p. 299.
4) Preliminary communication: see T.-S. Wu, T. Ohta, H. Furukawa, and C.-S. Kuoh, *Heterocycles*, **20**, 1267 (1983).
5) D. P. Chakraborty and B. K. Chowdhury, *J. Org. Chem.*, **33**, 1265 (1968).
6) W. Otting and G. Staiger, *Chem. Ber.*, **88**, 828 (1955).
7) H. J. Teuber and G. Staiger, *Chem. Ber.*, **89**, 489 (1956); *idem, ibid.*, **92**, 2385 (1959).
8) S. P. Lee and H. W. Moore, *Heterocycles*, **19**, 2019 (1982).
9) J. Bordner, D. P. Chakraborty, B. K. Choudhury, S. N. Ganguly, K. C. Das, and B. Weinstein, *Experientia*, **28**, 1406 (1972).
10) S. P. Kureel, R. S. Kapil, and S. P. Popli, *Experientia*, **25**, 790 (1969); *idem, Tetrahedron Lett.*, **1969**, 3857.
11) N. L. Dutta, C. Quassin, and M. S. Wadia, *Indian J. Chem.*, **7**, 1061 (1969).
12) D. P. Chakraborty, B. K. Barman, and P. K. Bose, *Tetrahedron*, **21**, 681 (1965).
13) D. P. Chakraborty, B. K. Barman, and P. K. Bose, *Science and Culture*, **30**, 445 (1964).
14) D. P. Chakraborty, K. C. Das, and P. K. Bose, *Science and Culture*, **32**, 83 (1966).
15) S. Roy, P. Bhattacharyya, and D. P. Chakraborty, *Phytochemistry*, **13**, 1017 (1974).
16) B. K. Chowdhury and D. P. Chakraborty, *Chem. Ind.* (London), **1969**, 549; *idem, Phytochemistry*, **10**, 1967 (1971).
17) S. P. Kureel, R. S. Kapil, and S. P. Popli, *Tetrahedron Lett.*, **1969**, 3857.

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