Alkaloidal Constituents of *Murraya koenigii*. Isolation and Structural Elucidation of Novel Binary Carbazolequinones and Carbazole Alkaloids

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Alkaloidal constituents of root and stem bark of *Murraya koenigii* (L.) SPRENG. (Rutaceae) grown in the greenhouse of Okitsu Branch, Fruit Tree Research Station, Shizuoka, were studied. Three new monomeric and five novel binary carbazole alkaloids named mukoenine-A (1), -B (2), and -C (4), and murrastifoline-F (8), bis-2-hydroxy-3-methylcarbazole (9), bismahanine (11), bikoeniquinone-A (12), and bismurrayaquinone-A (13), respectively, were isolated, as well as 16 kinds of known carbazoles and carbazolequinones, and their structures were elucidated by spectrometric methods. Among the new binary carbazoles, bikoeniquinone-A (12) and bismurrayaquinone-A (13) were found to contain a carbazole-1,4-quinone skeleton as a basic structural unit. These are the first examples of binary carbazolequinone alkaloids to be found in nature, and also the first carbazolequinone alkaloids to be isolated from *Murraya* plants except for *M. euchrestifolia*.

Keywords *Murraya koenigii*; carbazole; carbazolequinone; mukoenine; Rutaceae

The plant *Murraya koenigii* (L.) SPRENG. (Rutaceae) is a rich source of carbazole alkaloids.[1-3] Since the first isolation of carbazole alkaloids from this plant source,[1,4-6] many kinds of carbazole alkaloids have been obtained and their structures characterized. On the other hand, we have studied the constituents of *M. euchrestifolia* HAYATA grown in Taiwan[7] and found it to contain carbazolequinone alkaloids as well as carbazoles.[8,9] Carbazolequinones have so far been obtained only from *M. euchrestifolia*,[10] but not from *M. koenigii*. From a phytochemical viewpoint, we have therefore studied the alkaloidal constituents of *M. koenigii* cultivated in a greenhouse in Shizuoka, Japan.

This paper describes the isolation and structural elucidation of three new monomeric carbazoles named mukoenine-A (**1**), -B (**2**), and -C (**4**), three binary carbazoles named murrastifoline-F (**8**), bis-2-hydroxy-3-methylcarbazole (**9**), and bismahanine (**11**), and two novel binary carbazolequinones named bikoeniquinone-A (**12**) and bismurrayaquinone-A (**13**). This is the first report of the isolation of carbazolequinone alkaloids from a *Murraya* plant, except for *M. euchrestifolia*.

Results and Discussion

The acetone extract of the root or stem bark of the plant was fractionated by a combination of silica gel column chromatography (CC) and preparative TLC to give new alkaloids along with known carbazoles, as shown in Chart 1 and Chart 2, respectively.

Structure of Mukoenine-A (1) Mukoenine-A (**1**) was obtained as colorless prisms, mp 104—107 °C. The molecular formula was determined as $C_{18}H_{19}NO$ by high-resolution (HR)-MS. The UV spectrum showed typical absorption of a 2-oxygenated carbazole nucleus.[1,3] The IR spectrum showed bands at ν_{max} 3600 and 3460 cm^{-1} due to hydroxy and imino groups, respectively. The ^{1}H-NMR spectrum showed signals attributable to an aryl methyl [δ 2.40 (3H, s)] as well as an imino [δ 7.84 (1H, br s)] and a hydroxy group [δ 5.18 (1H, s)]. The presence of a prenyl group in the molecule was indicated by ^{1}H-NMR signals at δ 3.62 (2H, d, J=7.1 Hz), 5.37 (1H, t, J=7.1 Hz), 1.91 (3H, s), and 1.79 (3H, s) and a base fragment peak at m/z 209 [$M^+ - \cdot CH=C(CH_3)_2 - \cdot H$] in the electron impact (EI)-MS. In the aromatic proton region of the ^{1}H-NMR spectrum, a set of four-spin protons including a lower-field H-5 proton at δ 7.93 (1H, d, J=7.7 Hz) and a 1H-

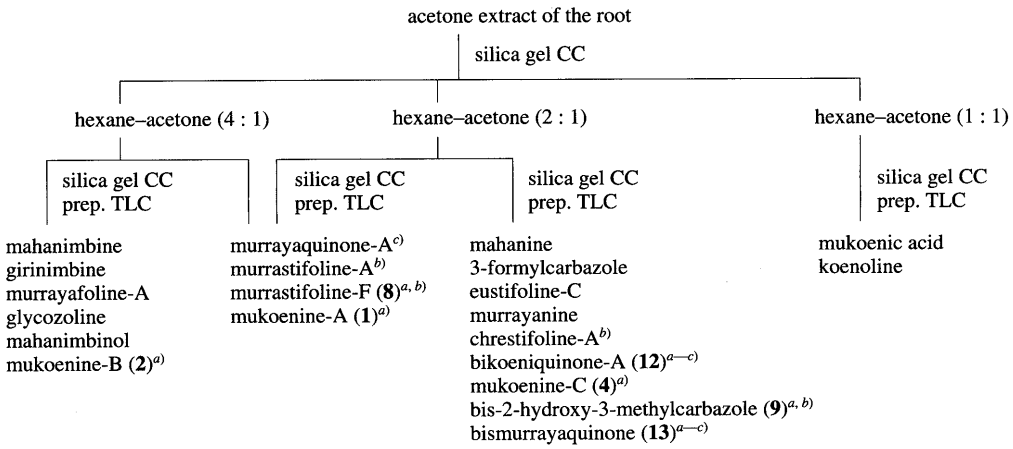

Chart 1. Isolation Procedure of Alkaloids from the Root of *Murraya koenigii*

a) New alkaloids. *b*) Binary alkaloids. *c*) Carbazolequinone alkaloids.

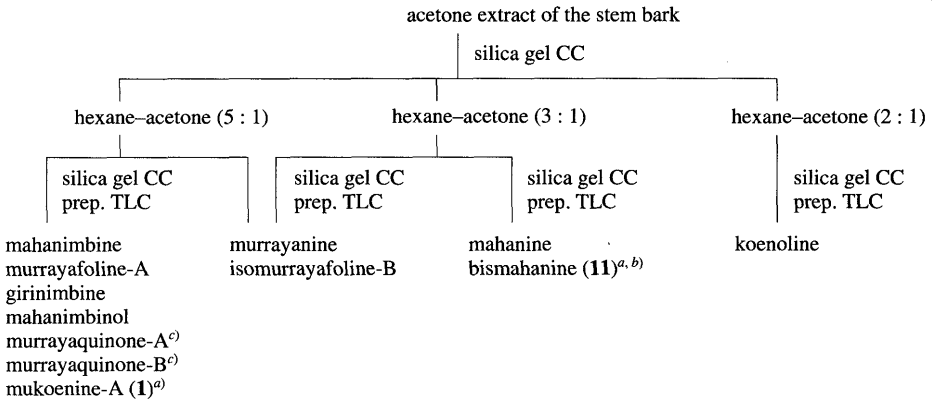

Chart 2. Isolation Procedure of Alkaloids from the Stem Bark of *Murraya koenigii*

a) New alkaloids. *b*) Binary alkaloids. *c*) Carbazolequinone alkaloids.

TABLE I. ^{1}H-NMR Data in $CDCl_3$

	1	2	4	8[a)]	9	11	12[a)]	13[a)]
H-2 (2′)	—	—	—	6.78 (s)		—	—	—
				7.05 (s)			6.94 (s)	
3 (3′)-R	2.40 (3H, s)	9.93 (s)	2.31 (3H, s)	2.52 (3H, s)	2.52 (6H, s)	2.33 (3H, s)	1.81 (3H, s)	2.08 (6H, s)
				2.05[b)]		2.31 (3H, s)	2.26 (3H, s)	
H-4 (4′)	7.68 (s)	8.07 (s)	7.55 (s)	7.71 (s)	7.99 (2H, s)	7.60 (s)	—	—
						7.54 (s)		
H-5 (5′)	7.93 (d, 7.7)	7.98 (d, 7.8)	7.72 (d, 8.1)	7.50 (d, 8.4)	8.03 (2H, d, 8.0)	7.84 (d, 8.3)	8.24 (d, 8.3)	8.23 (2H, d, 7.6)
				8.22 (d, 8.4)		7.89 (s)	7.72 (d, 8.3)	
H-6 (6′)	7.17 (t, 7.7)	7.26[b)]	6.68 (dd, 2.0, 8.1)	6.57 (t, 8.4)	7.22 (2H, t, 8.0)	6.95 (d, 8.3)	7.37 (t, 8.3)	7.39 (2H, t, 7.6)
				7.19 (t, 8.4)			7.23 (t, 8.3)	
H-7 (7′)	7.31 (t, 7.7)	7.38 (m)	—	7.17 (t, 8.4)	7.31 (2H, t, 8.0)	—	7.43 (t, 8.3)	7.47 (2H, t, 7.6)
				7.21 (t, 8.4)			6.89 (t, 8.3)	
H-8 (8′)	7.38 (d, 7.7)	7.38 (m)	6.81 (d, 2.0)	6.17 (d, 8.4)	7.23 (2H, d, 8.0)	—	7.65 (d, 8.3)	7.68 (2H, d, 7.6)
				6.74 (d, 8.4)		7.16 (s)	7.50 (d, 8.3)	
NH	7.84 (br s)	8.22 (br s)	7.76 (br s)	10.74 (br s)	7.64 (2H, br s)	7.95 (br s)	11.70 (br s)	11.79 (2H, s)
						7.57 (br s)	10.36 (br s)	
OH	5.18 (s)	11.66 (br s)	4.94 (br s)		5.27 (2H, s)	5.22 (br s)	—	—
						5.17 (br s)		
Others	5.37 (t, 7.1)	5.35 (t, 6.8)	6.58 (d, 9.7)	3.37 (3H, s)		6.67, 5.71 (d, 9.8)	4.01 (3H, s)	
	3.62 (2H, d, 7.1)	5.07 (m)	5.69 (d, 9.7)	4.11 (3H, s)		6.48, 5.55 (d, 9.8)		
	1.91 (3H, s)	3.67 (2H, d, 6.8)	1.47 (6H, s)			5.12, 5.08 (t, 6.8)		
	1.79 (3H, s)	2.10 (4H, m)				2.15 (4H, m)		
		1.91 (3H, s)				1.77, 1.71 (2H, m)		
		1.61 (3H, s)				1.66, 1.64, 1.59		
		1.57 (3H, s)				1.58, 1.46, 1.40		
						(each 3H, s)		

Values in (δ) ppm. The coupling constants (J) in parentheses are in Hz. All signals correspond to 1H, unless otherwise stated. *a*) Spectra were taken in acetone-d_6. *b*) Overlapped with the solvent signal.

singlet at δ 7.68, typical of a deshielded H-4,[1,3] suggested the presence of a nonsubstituted carbazole A-ring and a lone aromatic proton at C-4. In the nuclear Overhauser effect (NOE) experiment, irradiation of the aryl methyl signal at δ 2.40 showed an enhancement only at the H-4 signal, indicating the location of the aryl methyl, hydroxy, and prenyl groups at C-3, C-2, and C-1, respectively. These spectral data led to the structure **1** for mukoenine-A.

Structure of Mukoenine-B (2) This compound was isolated as a colorless oil, and its molecular formula was found to be $C_{23}H_{25}NO_2$ by HR-MS. The UV spectrum (see Experimental), IR band at ν_{max} 3470 cm^{-1}, and a D_2O-exchangeable signal at δ 10.51 and a set of four-spin protons at δ 8.04 (1H, d, J=7.8 Hz, H-5), 7.18 (1H, t, J=7.8 Hz, H-6), 7.33 (1H, t, J=7.8 Hz, H-7), and 7.44 (1H, d, J=7.8 Hz, H-8) in the ^{1}H-NMR (acetone-d_6) spectrum suggested the presence of a carbazole skeleton having no substituent at the A-ring. The presence of a formyl group which was strongly hydrogen-bonded with an *ortho*-located hydroxy group was indicated by an IR band at ν_{max} 1700 cm^{-1} and ^{1}H-NMR signals at δ 9.93 (1H, s, CHO) and 11.66 (1H, s, OH, D_2O-exchangeable). The location of the formyl group at C-3 was suggested by a lower chemical shift value (δ 8.07) of H-4 in the ^{1}H-NMR spectrum, which was deshielded by both the carbonyl group and the carbazole A-ring. Furthermore, the presence of a geranyl moiety in the molecule was shown by signals in the ^{1}H-NMR spectrum [δ 5.35 (1H, t, J=6.8 Hz), 5.07 (1H, m), 3.67 (2H, d, J=6.8 Hz), 2.10 (4H, m), 1.91 (3H, s), 1.61 (3H, s), 1.57 (3H, s)] and significant mass fragments at m/z 224 [$M^+ - \cdot CH=C(CH_3)CH_2-CH_2CH=C(CH_3)_2$] and 278 [$M^+ - \cdot CH_2CH=C(CH_3)_2$] in EI-MS. On the basis of these spectral data, we assigned the structure **2** to mukoenine-B.

Structure of Mukoenine-C (4) This alkaloid was obtained as a colorless oil, and its molecular formula was determined as $C_{18}H_{17}NO_2$ by HR-MS. The UV spectrum (see Experimental) and the ^{1}H-NMR signals at δ 5.69 (1H,

d, $J=9.7$ Hz), 6.58 (1H, d, $J=9.7$ Hz), 1.47 (6H, s) showed that this alkaloid has a pyranocarbazole nucleus in the molecule.[1,3] Two D_2O-exchangeable 1H broad singlets at δ 7.76 and 4.94 in the ^{1}H-NMR spectrum together with IR bands at ν_{max} 3460 and 3600 cm^{-1} were assigned to an NH and a hydroxy group, respectively. The presence of an aryl methyl group at C-3 and a lone aromatic proton at C-4 on the carbazole skeleton was shown by ^{1}H-NMR signals at δ 2.31 (3H, s) and 7.55 (1H, s), respectively, and by a 5% NOE enhancement between these proton signals. The hydroxy substituent at C-7 was suggested by the appearance of the remaining aromatic protons as a pair of ABC-type signals including an *ortho*-coupled lower-field H-5 proton signal (Table I). On the basis of these spectral data, we proposed the structure **4** for mukoenine-C.

Structure of Murrastifoline-F (8) Murrastifoline-F (**8**) was obtained as a colorless oil, and the molecular formula was proposed as $C_{28}H_{24}N_2O_2$ based on the HR-MS. The UV spectrum and IR bands at ν_{max} 3480 cm^{-1} due to an N–H group suggested the presence of a carbazole nucleus in the molecule. The ^{1}H-NMR spectrum showed singlet signals due to two aryl methyl, two methoxy, and three aromatic protons, together with an N–H group. Moreover, ^{1}H–^{1}H correlation spectrometry (COSY) in acetone-d_6 showed signals of two sets of four-spin proton systems, indicating the presence of two carbazole nuclei having no substituent on the A-ring. In the difference NOE experiments, irradiation of one of the aryl methyl signals at δ 2.55 gave 6 and 8% increases in the signals at δ 6.67 (H-2) and 7.67, characteristic of a lower field H-4 in the carbazole nucleus, respectively. On irradiation of one of the methoxy signals at δ 3.33, a 14% enhancement was observed at the signal of H-2. On the other hand, irradiations of another aryl methyl signal at δ 2.05 and a methoxy signal at δ 4.10 caused 5 and 12% enhancements, respectively, of the signal at δ 6.80 assignable to H-2′. Based on these data, the basic structural unit of **8** was concluded to be that of murrayafoline-A (**6**),[9] which co-occurs in the plant, and the position of the linkage of two molecules of **6** is between the *N*-atom of one unit and C-4′ of the second unit. These data confirmed the structure **8** for murrastifoline-F, a novel dimeric carbazole alkaloids of murrayafoline-A (**6**).

Structure of Bis-2-hydroxy-3-methylcarbazole (9) This compound was obtained as a colorless oil, and the molecular formula was determined as $C_{26}H_{20}N_2O_2$ by HR-MS. The ^{1}H-NMR spectrum showed an aryl methyl singlet (δ 2.52), a lower field 1H singlet (δ 7.99), and a set of four-spin proton signals [δ 8.03 (1H, d, $J=8.0$ Hz), 7.22 (1H, t, $J=8.0$ Hz), 7.31 (1H, t, $J=8.0$ Hz), 7.23 (1H, d, $J=8.0$ Hz)] together with two D_2O-exchangeable signals (δ 7.64, 5.27). The number of these signals was half of that expected, suggesting that this compound has a completely symmetrical structure. The similarity of the UV spectrum of this compound to that of 2-hydroxy-3-methylcarbazole (**3**)[11] coupled with the ^{1}H-NMR results described above, suggested the presence of 2-hydroxy-3-methylcarbazole as structural units. An 8% NOE enhancement of a lower singlet at δ 7.99 due to H-4 on irradiation of the aryl methyl signal in the difference NOE experiment and the lack of a signal due to H-1 in the ^{1}H-NMR spectrum indicated the position of the linkage between the two carbazole units to be at C-1. On the basis of these spectral data, we propose the structure of this alkaloid to be represented by formula **9**.

Bismahanine (11) This compound was isolated as a colorless oil. The molecular formula, $C_{46}H_{48}N_2O_4$, was established by HR-MS. The ^{1}H-NMR spectrum showed signals due to two aryl methyls (δ 2.33, 2.31), imino (δ 7.95, 7.57), and hydroxy groups (δ 5.22, 5.17). A dimeric structure of carbazole nuclei having methylpyran rings with 1,1-dimethyl-1-butene [$-CH_2CH_2CH=C(CH_3)_2$] moieties as side chains was suggested by the following spectral data. a) The good resemblance of the UV spectrum of **11** with that of a known monomeric carbazole, mahanine (**5**).[12] b) ^{1}H-NMR signals at δ 5.12 (1H, t, $J=6.8$ Hz), 5.08 (1H, t, $J=6.8$ Hz), 2.15 (4H, m), 1.77 (2H, m), 1.71 (2H, m), together with six methyl singlets and two pairs of AB-type signals at δ 6.67 and 5.71 (each 1H, d, $J=9.8$ Hz) and δ 6.48 and 5.55 (each 1H, d, $J=9.8$ Hz). c) Mass fragment ions at *m/z* 609 [$M^+ - \cdot CH_2{-}CH=C(CH_3)_2 - \cdot CH_3 + \cdot H$], 347 [$1/2M^+ + 1$], and 263 [$1/2(M^+ - C_6H_{11})$]. In the aromatic proton region of the ^{1}H-NMR spectrum of **11**, a pair of *ortho*-coupled protons at δ 7.84 and 6.95 (each 1H, d, $J=8.3$ Hz) assignable to H-5 and H-6, respectively, and four 1H singlets were observed. Among these four singlets, signals at δ 7.60 and 7.54, which were found to have long-range coupling with the aryl methyls at δ 2.33 and 2.31, respectively, by means of decoupling experiments were assigned to protons (H-4 and 4′) *ortho*-located to the aryl methyls. The lowest-field singlet at δ 7.89 could be assigned to H-5′ and the remaining singlet at δ 7.16 to H-8′ in the carbazole nucleus. On the basis of these data coupled with the good similarity of the signal pattern and chemical shift values in the ^{1}H-NMR (acetone-d_6) spectrum to those of bis-7-hydroxygirinimbine-B (**10**),[13] except for signals due to the side chain, we assigned the structure of bismahanine as **11**.

Structure of Bikoeniquinone-A (12) Bikoeniquinone-A (**12**) was isolated as an orange oil, and the molecular formula, $C_{27}H_{20}N_2O_3$, was determined by HR-MS. The ^{1}H-NMR spectrum (acetone-d_6) coupled with the results of ^{1}H–^{1}H COSY showed the presence of two sets of four-spin proton systems along with a lone proton (δ 6.94) in the aromatic proton region, two methyls attached to sp^2 carbons, a methoxy group and two D_2O-exchangeable protons (δ 11.70, 10.36) due to N–H groups. The structure of **12** including murrayaquinone-A (**7**)[8] and murrayafoline-A (**6**)[9] units in the molecule was suggested by the following spectral data. a) A strong absorption band at ν_{max} 1645 cm^{-1} in the IR spectrum. b) Typical UV bands at λ_{max} 227, 240, 257, 289, and 331 nm.[8,9] c) Mass fragment at *m/z* 211 ($C_{14}H_{13}NO$) corresponding to the lower carbazole unit of **12**. d) Observation of 8 and 14% NOE enhancements of H-2′ (δ 6.94) on irradiations of the aryl methyl (δ 2.26) and the methoxy (δ 4.01) protons, respectively. Lack of lone proton signals at δ 6.52 and 7.49 in the ^{1}H-NMR (acetone-d_6) spectra of **7**[8,9] and **6**,[8,9] respectively, and observation of NOE enhancements between two methyl singlets (δ 1.81, 2.26) indicated the position of the linkage between **7** and **6** to be at C-2 and C-4, respectively. On the basis of these spectral data, we proposed the structure **12** for bikoeniquinone-A.

Structure of Bismurrayaquinone-A (13) This compound was obtained as an orange powder and its molecular formula was proposed to be $C_{26}H_{16}N_2O_4$ on the basis of

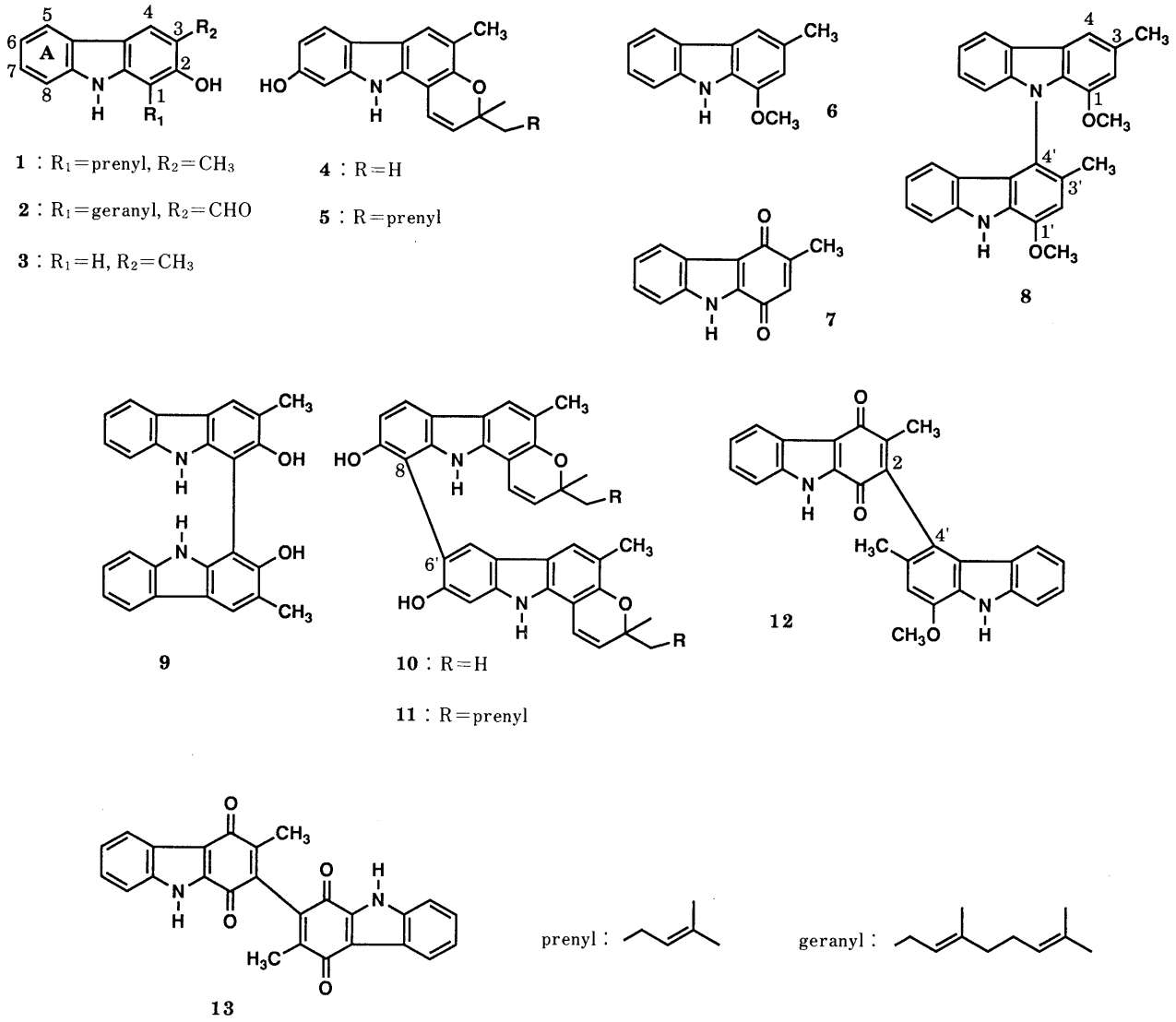

Fig. 1

HR-MS analysis. The ^{1}H-NMR (acetone-d_6) spectrum showed a simple signal pattern assignable to a set of four-spin proton signals, an aryl methyl singlet, and an N–H broad signal (Table I). Good resemblance of the UV and ^{1}H-NMR spectra to those of murrayaquinone-A (**7**),[8,9] except for the lack of a signal due to H-2 in the spectrum of **7**, coupled with a strong IR band at ν_{max} 1650 cm^{-1} suggested the structure **13** corresponding to a dimer of murrayaquinone-A (**7**).

Other carbazolequinones and carbazole alkaloids isolated from the plant material were characterized as murrayaquinone-A and -B,[8,9] mahanimbine,[9] murrayafoline-A,[9] glycozoline,[14] girinimbine,[9] mahanimbinol,[15] mahanine,[12] 3-formylcarbazole,[8] murrayanine,[9] mukoenic acid,[9] koenoline,[16] isomurrayafoline-B,[17] eustifoline-C,[18] murrastifoline-A,[19] and chrestifoline-A[19] by comparison of ^{1}H-NMR and IR spectra with those of authentic samples or spectroscopic data described in the literature.[14,16]

Experimental

Melting points were measured on a micromelting point hot-stage apparatus (Yanagimoto). ^{1}H-NMR spectra were recorded on GX-270 (JEOL) or GX-400 (JEOL) spectrometer in $CDCl_3$, unless otherwise stated. Chemical shifts are shown in δ values (ppm) with tetramethylsilane (TMS) as an internal reference. All MS were taken under EI conditions using an M-80 (Hitachi) or a JMS-HX-110 (JEOL) spectrometer having a direct inlet system. UV spectra were recorded on a UVIDEC-610C double-beam spectrophotometer (JASCO) in methanol, and IR spectra on an IR-810 (JASCO) in $CHCl_3$. Preparative TLC was done on Kieselgel 60 F_{254} (Merck).

Extraction and Isolation The plant material used in this study, *Murraya koenigii* (L.) SPRENG., was grown in a greenhouse at the Okitsu Branch, Fruit Tree Research Station, Ministry of Agriculture, Forestry and Fisheries, Shimizu, Shizuoka (Saga Univ. Acc. No. 78045). The seed of this plant was provided by Prof. Masao Iwamasa, Saga University.

a) From the Root: The acetone extract of dried root (220 g) was treated by the procedure shown in Chart 1. The acetone extract was chromatographed over silica gel with hexane–acetone (10 : 1, 4 : 1, 2 : 1, 1 : 1), acetone, and methanol, successively to give 12 fractions. Each fraction was further subjected to silica gel CC and preparative TLC to obtain mahanimbine (2.5 mg), murrayafoline-A (3 g), glycozoline (2 mg), girinimbine (357 mg), mukoenine-B (**2**) (2.4 mg), murrayaquionone-A (66 mg), murrastifoline-A (3.7 mg), mahanimbinol (19 mg), murrastifoline-F (**8**) (3.7 mg), mukoenine-A (**1**) (19.4 mg), mahanine (2.5 mg), 3-formylcarbazole (1.6 mg), eustifoline-C (1.1 mg), murrayanine (125 mg), bis-2-hydroxy-3-methylcarbazole (**9**) (3 mg), chrestifoline-A (3 mg), bikoeniquinone-A (**12**) (2.4 mg), bismurrayaquinone (**13**) (2.2 mg), mukoenine-C (**4**) (5.3 mg), mukoenic acid (1.8 mg), and koenoline (5 mg).

b) From the Stem Bark: The acetone extract of the stem bark (120 g) of the plant was treated by an analogous procedure to a) described above to isolate mahanimbine (37 mg), murrayafoline-A (3 mg), girinimbine

(18 mg), mahanimbinol (51 mg), murrayaquinone-A (2.5 mg), murrayaquinone-B (1.7 mg), isomurrayafoline-B (3.7 mg), mukoenine-A (**1**) (3.1 mg), murrayanine (13 mg), mahanine (14 mg), bismahanine (**11**) (2.5 mg), and koenoline (1.5 mg).

Mukoenine-A (1) Colorless prisms, mp 104—107 °C. UV λ_{max} nm: 217, 238, 260 (sh), 288, 300, 321 (sh), 333, 356. IR ν_{max} cm^{-1}: 3600, 3460, 1615. EI-MS *m/z* (%): 265 (M^+, 60), 250 (10), 248 (14), 210 (72), 209 (100), 180 (38), 167 (19). NOE: irradiation of 3-CH_3 (δ 2.40), 5% enhancement of H-4 (δ 7.68). HR-MS Calcd for $C_{18}H_{19}NO$: 265.1465. Found: 265.1459.

Mukoenine-B (2) Colorless oil. UV λ_{max} nm: 222, 238, 284 (sh), 294, 331, 342 (sh), 360 (sh). IR ν_{max} cm^{-1}: 3470 (br), 1700, 1640, 1610. ^{1}H-NMR (acetone-d_6) δ: 11.72 (1H, s, OH), 10.51 (1H, br s, NH), 9.94 (1H, s, CHO), 8.31 (1H, s, H-4), 8.04 (1H, d, J=7.8 Hz, H-5), 7.44 (1H, d, J=7.8 Hz, H-8), 7.33 (1H, t, J=7.8 Hz, H-7), 7.18 (1H, t, J=7.8 Hz, H-6), 5.34 (1H, t, J=6.8 Hz), 4.99 (1H, m), 3.61 (2H, d, J=6.8 Hz), 2.00 (4H, overlapped with solvent), 1.80 (3H, s), 1.49 (3H, s), 1.46 (3H, s). EI-MS *m/z* (%): 347 (M^+, 35), 331 (5), 278 (29), 262 (13), 248 (32), 236 (6), 224 (68), 211 (11), 180 (13), 167 (24). HR-MS Calcd for $C_{23}H_{25}NO_2$: 347.1883. Found: 347.1874.

Mukoenine-C (4) Colorless oil. UV λ_{max} nm: 204, 234, 248 (sh), 278, 288, 298, 325 (sh), 343. IR ν_{max} cm^{-1}: 3600, 3460, 1625, 1610. EI-MS *m/z* (%): 279 (M^+, 41), 264 (100), 197 (11), 132 (19). HR-MS Calcd for $C_{18}H_{17}NO_2$: 279.1258. Found: 279.1253. Difference NOE: Irradiation of 3-CH_3 (δ 2.31), 5% enhancement of H-4 (δ 7.55).

Murrastifoline-F (8) Colorless oil. UV λ_{max} nm: 227, 243, 253 (sh), 282, 292, 332, 346. IR ν_{max} cm^{-1}: 3480 (NH), 1590. ^{1}H-NMR δ: 8.27 (1H, br s, NH), 8.16 (1H, d, J=8.4 Hz, H-5′), 7.67 (1H, s, H-4), 7.36 (1H, d, J=8.4 Hz, H-5), 7.17—7.26 (3H, overlapped signals), 6.88 (1H, s, H-8′), 6.80 (1H, d, J=8.4 Hz, H-2′), 6.67 (1H, s, H-2), 6.64 (1H, t, J=8.4 Hz, H-6), 6.29 (1H, d, J=8.4 Hz, H-8), 4.10 (3H, s, 1′-OCH_3), 3.33 (3H, s, 1-OCH_3), 2.55 (3H, s, 3-CH_3), 2.05 (3H, s, 3′-CH_3). EI-MS *m/z* (%): 420 (M^+, 100), 405 (11), 211 (13), 210 (42), 167 (11). HR-MS Calcd for $C_{28}H_{24}N_2O_2$: 420.1836. Found: 420.1866.

Bis-2-hydroxy-3-methylcarbazole (9) Colorless oil. UV λ_{max} nm: 214, 237, 260 (sh), 304, 336. IR ν_{max} cm^{-1}: 3530, 3450, 1610. EI-MS *m/z* (%): 392 (M^+, 100), 196 (61), 167 (18). HR-MS Calcd for $C_{26}H_{20}N_2O_2$: 392.1523. Found: 392.1525. Calcd for $C_{13}H_{10}NO$: 196.0762. Found: 196.0773. Difference NOE: Irradiation of 3 (3′)-CH_3 (δ 2.52), 8% enhancement of H-4 (δ 7.99).

Bismahanine (11) Colorless oil. UV λ_{max} nm: 223, 245, 297, 331, 341 (sh), 359 (sh). IR ν_{max} cm^{-1}: 3540, 3460, 1610. ^{1}H-NMR (acetone-d_6) δ: 9.69 (1H, s), 7.82 (1H, s), 7.77 (1H, d, J=8.4 Hz), 7.63 (2H, s), 7.04 (1H, s), 6.96 (1H, d, J=10.1 Hz), 6.87 (1H, d, J=10.1 Hz), 6.85 (1H, d, J=8.4 Hz), 5.77 (1H, d, J=10.1 Hz), 5.55 (1H, d, J=10.1 Hz), 5.14 (2H, br s), 2.30 (3H, s), 2.15 (2H, m), 1.7—1.8 (4H, m), 1.63 (3H, s), 1.60 (3H, s), 1.56 (3H, s), 1.54 (3H, s), 1.46 (3H, s), 1.39 (3H, s). One of the aryl methyl signals may overlap the solvent signal. EI-MS *m/z* (%): 692 (M^+, 100), 609 (56), 558 (16), 525 (8), 475 (20), 347 (21), 263 (49). HR-MS Calcd for $C_{46}H_{48}N_2O_4$: 692.3611. Found: 692.3666.

Bikoeniquinone (12) Orange oil. UV λ_{max} nm: 227, 240, 257 (sh), 289, 331. IR ν_{max} cm^{-1}: 3460, 3430, 1645. ^{1}H-NMR δ: 9.48 (1H, br s), 8.36 (1H, d, J=8.1 Hz), 8.30 (1H, br s), 7.75 (1H, d, J=8.1 Hz), 7.3—7.45 (5H, overlapped signals), 6.97 (1H, t, J=8.1 Hz), 6.86 (s), 4.05 (3H, s), 2.29 (3H, s), 1.93 (3H, s). EI-MS *m/z* (%): 420 (M^+, 100), 405 (71), 390 (14), 362 (7), 333 (6), 306 (5), 248 (21), 211 (15), 210 (17), 204 (19), 167 (20). HR-MS Calcd for $C_{27}H_{20}N_2O_3$: 420.1472. Found: 420.1465. Calcd for $C_{14}H_{13}NO$: 211.0995. Found: 211.0989. Difference NOE: Irradiation of 3-CH_3 (δ 1.81), 3% enhancements of 3′-CH_3 (δ 2.26) and H-5′ (δ 7.72). Irradition of 3′-CH_3 (δ 2.26), 2 and 8% enhancements of 3-CH_3 (δ 1.81) and H-2′ (δ 6.94), respectively. Irradiation of 1′-OCH_3 (δ 4.01), 14% enhancement of H-2′ (δ 6.94).

Bismurrayaquinone-A (13) Orange powder. UV λ_{max} nm: 225, 243, 252, 260 (sh), 280 (sh), 291, 330, 343, 392. IR ν_{max} cm^{-1}: 3440, 1710, 1650, EI-MS *m/z* (%): 420 (M^+, 100), 405 (79), 392 (15), 391 (27), 377 (12), 375 (12), 264 (3), 248 (9), 211 (10), 210 (11). HR-MS Calcd for $C_{26}H_{16}N_2O_4$: 420.1108. Found: 420.1105.

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