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SEASONAL VARIATIONS OF CARBAZOLE ALKALOIDS IN *MURRAYA EUCHRESTIFOLIA*

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Key Word Index—*Murraya euchrestifolia*; Rutaceae; leaves; carbazole alkaloid; murrayamines F–H; euchrestifoline.

Abstract—Four new carbazole alkaloids, murrayamines F–H and euchrestifoline, were isolated from the leaves of *Murraya euchrestrifolia* in May. The variation of carbazole alkaloids in the leaves with seasons was also examined and the results obtained could be used to explain that the pharmacological activity of the plant in traditional Chinese medicines is strictly related to the collection time. Neither coumarins nor flavonoids were found in *M. euchrestifolia* and supported Tanaka's proposition to divide *Murraya* into two sections, *Murraya* and *Bergera*.

INTRODUCTION

Plants of the genus *Murraya* growing naturally in Southern Asia are shrubs up to 4–5 m high [1]. Extracts of the leaves and bark have been used as a folk medicine for analgesia and local anesthesia, and for treatment of eczema, rheumatism, dropsy, abdominal pain, stomach-ache, toothache, diarrhoea, oedema, thrombosis and stasis of blood, and as an expectorant, anticonvulsant, anodyne and detoxification agent [2].

The chemical constituents of the genus *Murraya* have been extensively investigated since 1965 [3–6]. It is apparent that plants rich in coumarins and flavonoids contain little or no carbazole alkaloids, whereas those rich in carbazole alkaloids seldom contain coumarins or flavonoids [7–9].

We have shown the occurrence of numerous new monomeric and dimeric carbazole alkaloids in *M. euchrestifolia* from fruits [10], roots and stem barks [11–30], and also the leaves collected in summer [31], autumn [32] and winter [33, 34]. In continuation of our phytochemical study on the constituents of the leaves of this species collected in spring (May), four new carbazole alkaloids, murrayamines F–H (**1–3**) and euchrestifoline (**4**) were isolated. We describe the isolation and structural elucidation of these new compounds and discuss the constitutional variation of carbazole alkaloids according to season.

RESULTS AND DISCUSSION

Fractionation of the acetone extract of leaves of *M. euchrestifolia* resulted in the isolated of the four new carbazole alkaloids, along with four known carbazole alkaloids, murrayazoline (**5**) [18], girinimbine (**6**) [18], murrayazolidine (**7**) [18] and murrayazolinine (**8**) [35], together with a steroid mixture (**9**).

Murrayamine F (**1**), an oil, was determined to have the molecular formula $C_{24}H_{27}NO_2$ by high-resolution mass measurement. The UV bands at 221, 244, 256 (sh), 303, 316 (sh), 328 (sh) nm revealed this compound to be a 1,7-dioxygenated carbazole derivative [31]. Inspection of the ^{1}H NMR spectrum of compound **1** (Table 1) allowed several signals could be readily assigned: *ortho*-coupled doublets for H-5 and H-6 at δ 7.69 and 6.70 ($J = 8.4$ Hz), *meta*-coupled protons appearing as broadened singlets at δ 6.62 and 7.32 for H-2 and H-4, respectively. An aromatic methyl singlet at δ 2.49 was attached to C-3 and an aromatic methoxyl singlet δ 3.97 should be at C-1. The NOE difference spectrum provided information about the location of those substituents on ring C. The 10.69% and 6.84% enhancements for the signals at δ 7.32 (H-4) and 6.62 (H-2) were observed an irradiation of the methyl signal at δ 2.49 (3-Me). Furthermore, only the signal at δ 6.62 could be increased by 17.3% after irradiation of the methoxyl signal at δ 3.97 (1-OMe). The peaks in the upfield region of compound **1** were similar to those of murrayazolidine (**7**), which has also been isolated from this species. Two vinylidene protons appeared as typical broadened singlets at δ 4.69 and 4.79. In addition, the peak at δ 3.45 (1H, *m*) was attributed to benzylic protons, (H-1′). In the ^{1}H NMR region δ 1.5–2.6, multiplicities of these signals suggested the existence of three methylene and one methine protons, which were supported by a decoupling experiment. Finally, the spectrum contained two more three-proton singlets at δ 1.55 for vinyl methyl and 1.42 for a

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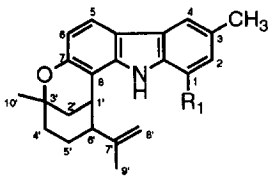
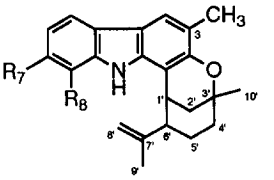
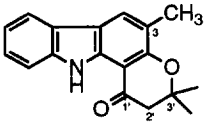


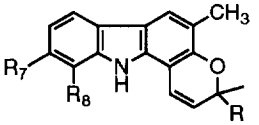
Murrayamine-F (**1**) : $R_1 = OCH_3$
Murrayamine-G (**2**) : $R_1 = H$



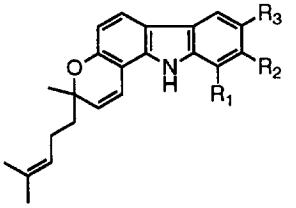
Murrayamine-H (**3**) : $R_7 = H$, $R_8 = OCH_3$
Murrayazolidine (**7**) : $R_7 = H$, $R_8 = H$
Murrayamine-D : $R_7 = OH$, $R_8 = H$



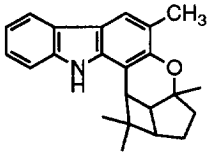
Euchrestifoline (**4**)



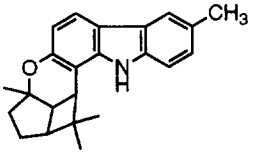
Murrayamine-A : $R_7 = OH$, $R_8 = H$, $R = CH3$
Murrayamine-B : $R_7 = H$, $R_8 = OCH_3$, $R = CH_2CH_2CH=(CH_3)_2$
Murrayamine-I : $R_7 = OH$, $R_8 = H$, $R = CH_2OAc$
Murrayamine-K : $R_7 = H$, $R_8 = H$, $R = CH_2OAc$
Girinimbine (**6**) : $R_7 = H$, $R_8 = H$, $R = CH_3$
Mahanimbine : $R_7 = H$, $R_8 = H$, $R = CH_2CH_2CH=(CH_3)_2$
(+)-Mahanine : $R_7 = OH$, $R_8 = H$, $R = CH_2CH_2CH=(CH_3)_2$



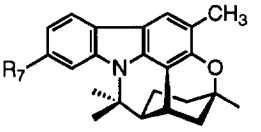
Murrayamine-C : $R_1 = OCH_3$, $R_2 = H$, $R_3 = CH_3$
Murrayamine-J : $R_1 = H$, $R_2 = H$, $R_3 = CHO$
Murrayamine-N : $R_1 = OCH_3$, $R_2 = H$, $R_3 = CHO$
Isomahanine : $R_1 = H$, $R_2 = OH$, $R_3 = CH_3$



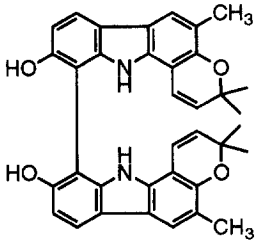
Bicyclomahanimbine



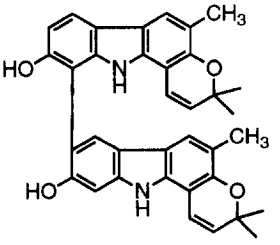
Murrayamine-M



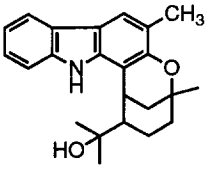
Murrayamine-E : $R_7 = OH$
Murrayazoline (**5**) : $R_7 = H$



Bis-7-hydroxygirinimbine-A



Bis-7-hydroxygirinimbine-B



Murrayazolinine (**8**)

methyl in a geminal position to the electronegative oxygen substituents. These results inferred a 10-carbon bicylic ring containing methyl and isopropenyl substituents fused to the A-ring of a carbazole nucleus. Consequently, the pentacyclic structure of murrayamine F was deduced as compound **1**.

Murrayamine G (**2**) was isolated as needles and the molecular formula was determined as $C_{23}H_{25}NO$, OCH_2 less than that of **1**. H was deduced as a-7-oxygenated carbazole alkaloid derivative because of the UV absorptions at 221, 241, 262 and 307 nm [36]. The absence of the methoxyl signal and an AB-type pattern at δ 6.72 and 7.72 (*d*, $J = 8.3$ Hz, H-6 and H-5, respectively) and an ABX spin system at δ 7.10 (*dd*, $J = 8.3$, 1.0 Hz, H-2), 7.22 (*d*, $J = 8.3$ Hz, H-1) and 7.71 (*br s*, H-4), and also a typical aromatic methyl at δ 2.49 on C-3 in the ^{1}H NMR spectrum of compound **2** constructed a 3-methyl-7-oxygenated-8-alkylcarbazole unit (Table 1). That irradiation of the methyl singlet at δ 2.49 gave rise to 8.3% and 10.6% increases of the signals at δ 7.10 (H-2) and 7.71 (H-4), respectively, further confirmed the presence of this unit. The similarity of the vinyl protons and aliphatic protons in compound **2** to those in compound **1** revealed a 10-carbon bicyclic ring connected to the A-ring of carbazole. These results led us to propose structure **2** for murrayamine G.

Murrayamine H (**3**) is an isomer of **1**. All the

Table 1. ^{1}H NMR spectra data of compounds **1**–**4*** (400 MHz, in $CDCl_3$; *J* (Hz) values in parentheses)

	1	2	3	4
H-1 or 1-OMe	3.97 *s*	7.22 *d* (8.3)	–	–
H-2	6.62 *br s*	7.10 *dd* (8.3, 1.0)	–	–
3-Me	2.49 *s*	2.49 *s*	2.33 *s*	2.39 *d* (0.7)
H-4	7.32 *br s*	7.71 *br s*	7.61 *br s*	8.02 *q* (0.7)
H-5	7.69 *d* (8.4)	7.72 *d* (8.3)	7.50 *dd* (7.8, 1.2)	7.95 *br d* (8.2)
H-6	6.70 *d* (8.4)	6.72 *d* (8.3)	7.06 *t* (7.8)	7.23 *ddd* (8.2, 7.2, 0.9)
H-7	–	–	6.78 *dd* (7.8, 1.2)	7.39 *ddd* (8.2, 7.2, 0.9)
H-8 or 8-OME			3.99 *s*	7.48 *dd* (8.2, 0.9)
NH	7.88 *br s*	7.,71 *br s*	7.90 *br s*	10.14 *br s*
H-1′	3.45 *m*	3.41 *br d* (3.0)	3.48 *m*	–
H-2′	1.93 *dt* (12.8, 2.4)	1.95 *ddd*	1.90 *dt* (13.4, 2.8)	2.83 *s*
	2.03 *dd* (12.8, 2.4)	(12.6, 3.0, 1.2)	2.04 *dd* (13.4, 2.8)	
		2.03 *dd* (12.6, 3.0)		
3′-Me	1.42 *s*	1.43 *s*	1.43 *s*	1.54 *s*
H-4′	1.62 *dt* (9.3, 2.4)	1.66 *br d* (12.6)	1.61 and 2.10 *m*	–
	2.10 *dt* (9.3, 2.4)	2.10 *dd* (12.6, 2.4)		
H-5′	1.48 *m*	1.50 *m*	1.46 & 1.70 *m*	–
	1.66 *dt* (9.3, 2.4)	1.70 *dt* (12.6, 2.4)		
H-6′	2.53 *m*	2.57 *dd* (9.0, 2.4)	2.58 *m*	–
7′-Me (H-9′)	1.55 *s*	1.50 *s*	1.56 *s*	–
H-8′	4.69 & 4.79 *br s*	4.73 and 4.81 *br s*	4.17 & 4.80 *br s*	–

substituents, including an aromatic methyl at δ 2.33 (*s*), an aromatic methoxyl at δ 3.99 (*s*), a bicyclic ring with isopropenyl and methyl substituents in ^{1}H NMR spectrum of compound **3** were in agreement with those of compound **1** (Table 1); the difference between them was in the location of these groups. According to the chemical shift and splitting pattern of the signals in the aromatic region, a lone proton at δ 7.61 (*s*) was assigned to H-4 and the mutually coupled ABX pattern at δ 6.78 (*dd*, J = 7.8, 1.2 Hz), 7.06 (*t*, J = 7.8 Hz), and 7.50 (*dd*, J = 7.8, 1.2 Hz) was attributed to H-7, H-6 and H-5, respectively. The methoxyl substituent should positioned at C-8 because of the downfield shift of H-5 (δ 7.50). A NOE difference experiment showed enhancement of the signal at δ 7.61 (H-4) by 10.9% during irradiation of the signal at δ 2.33 (3-Me), whereas an increase of H-7 (δ 6.78) by 10.5% after irradiation of 8-OMe (δ 3.99) was observed. These spectral data supported the structure of murrayamine H as compound **3**.

Euchrestifoline (**4**) was obtained as yellow needles with a molecular formula of $C_{18}H_{17}NO_2$. Except for a methyl group (δ 2.39) at C-3, the ^{1}H NMR spectrum of compound **4** clearly showed that the molecule contained a singlet proton at δ 8.02 for H-4 and four mutually coupled protons at δ 7.23 (*ddd*, J = 8.2, 7.2, 0.9 Hz, H-6), 7.39 (*ddd*, J = 8.2, 7.2, 0.9 Hz, H-7), 7.48 (*dd*, J = 8.2, 0.9 Hz, H-8) and 7.95 (*br d*, J = 8.2 Hz, H-5) for a nonsubstituted A-ring carbazole (Table 1). A relatively low-field broad signal at δ 10.14 along with the IR absorptions at 3440 (NH) and 1650 (C=O) cm^{-1} suggested that compound **4** would be a keto-carbazole with intramolecular hydrogen bonding. The remaining signals, including two methyls at δ 1.54 (*S*) adjacent to an oxygen functionality and a methylene at δ 2.83 (*s*), represented a dimethyl pyranone ring fused to the C-ring. On the basis of these data, the structure of euchrestifoline was proposed to be compound **4**.

This work and our previous results show that the constitutions of the leaves of *M. euchrestifolia* vary according to season (Table 2). Girinimbine (**6**) occurs in all seasons; the dimeric carbazole alkaloids, bis-7-hydroxygirinimbine-A and bis-7-hydroxygirinimbine-B, were found only in winter; pentacyclic carbazole alkaloids with terminal methylene substitution, murrayamines D, F (**1**), G (**2**), and H (**3**), murrayazolidine (**7**) and murrayazolinine (**8**), existed in spring, whereas the methyl at C-3 in some of the carbazole alkaloids, such as murrayamines J, M and N, was oxidized to aldehyde or the methyl of the 2,2-dimethylpyran ring, as in murrayamines I and K, was oxidized to alcohol in the autumn. This is the reason why the pharmacological activity of this species traditional Chinese medicine is related strictly to the collection time.

Ecologically, species, such as *M. exotica* and *M. paniculata*, rich in coumarins and flavonoids were found to contain no carbazole alkaloids, whereas others, such as *Murraya*, *Clausena*, *Glycosmis* and *Micromelium*, were rich in carbazole alkaloids but had no coumarins or flavonoids. Neither coumarins nor flavonoids were found in *M. euchrestifolia* and support Tanaka's proposition to divide *Murraya* into two sections, *Murraya* and *Bergera*, which differ from each other in both external morphology and chemical constitution [7–9, 37, 38].

EXPERIMENTAL

General. Mps: uncorr. UV: MeOH. IR: $CHCl_3$. ^{1}H and ^{13}C NMR: $CDCl_3$ with TMS as int. ref. MS: direct inlet.

Plant material. Leaves of *M. euchrestifolia* Hayata

Table 2. Variation of alkaloid content in leaves of *Murrya euchrestifolia*

	Compound	February	May	August	November	Ref.
C_{18}	Girinimbine (**6**)	++	+	++	++	31, 32, 36
unit	Murrayamine-A	+	−	++	+	31, 32, 36
	Murrayamine-I	−	−	−	+	32
	Murrayamine-K	−	−	−	+	32
	Euchrestifoline (**4**)	−	+	−	−	This work
C_{23}	Murrayazoline (**5**)	−	+	−	−	This work
unit	Murayazolidine (**7**)	−	++	−	−	This work
	Murrayazolinine (**8**)	−	+	−	−	This work
	Bicyclomahanimbine	+	−	−	+	32, 36
	Mahanimbine	++	−	++	++	31, 32, 36
	(+)-Mahanine	+	−	++	+	31, 32, 36
	Murrayamine-B	−	−	+	−	31
	Murrayamine-C	−	−	+	−	31
	Murrayamine-D	+	−	−	+	32, 36
	Murrayamine-E	+	−	−	+	32, 36
	Murrayamine-F (**1**)	−	+	−	+	This work
	Murrayamine-G (**2**)	−	+	−	−	This work
	Murrayamine-H (**3**)	−	+	−	−	This work
	Murrayamine-J	−	−	−	+	32
	Murrayamine-M	−	−	−	+	32
	Murrayamine-N	−	−	−	+	32
	Isomahanine	−	−	−	+	32
Dimer	bis-7-Hydroxygirinimbine-A	+	−	−	−	33
	bis-7-Hydroxygirinimbine-B	+	−	−	−	33
	Unknown dimer C	+	−	−	−	−
	Unknown dimer D	−	−	−	+	−

+, Content < 100 mg/kg; ++, content > 100 mg/kg; −, no isolation.

were collected in Kuantaochi, Nantou Hsien, Taiwan, in May 1986 and identified by Prof. C. S. Kuoh. A specimen of the plant has been deposited at the herbarium of the National Cheng Kung University, Tainan, Taiwan.

Extraction and isolation. Air-dried leaves (0.43 kg) were extracted with Me_2CO at room temp. The combined Me_2CO extracts were concd under red. pres. to yield a dark-brown syrup (32 g) which was subjected to CC over silica gel and eluted with benzene–Me_2CO (9:1) to give 10 frs. Fr. 1 was repeatedly rechromatographed by silica gel CC to furnish compounds **9** (1.1 g), **1** (6 mg), **5** (3 mg), **2** (9 mg), **3** (3 mg), **6** (0.1 g) and **7** (174 mg), successively. Fr. 5 was also rechromatographed on silica gel to give compounds **8** (12 mg) and **4** (4 mg).

Murrayamine F (**1**). Oil. HRMS: calcd for $C_{24}H_{27}NO_2$, *m/z* 361.2041 $[M]^+$, found 361.2043. UV λ_{max} nm 221, 244, 256 (sh), 303, 316 (sh), 328 (sh). IR ν_{max} cm^{-1}: 3649, 1622, 1585. EIMS *m/z* (rel. int.): 361 ($[M]^+$, 69), 278 (100), 263 (14), 240 (17)).

Murrayamine G (**2**). Needles, mp 173–176° (MeOH). HRMS: calcd for $C_{23}H_{25}NO$, *m/z* 331.1934 $[M]^+$, found 331.1920. UV λ_{max} nm 221, 241, 262, 303, 307. IR ν_{max} cm^{-1}: 3465, 1617. EIMS *m/z* (rel. int.): 331 ($[M]^+$, 38), 316 (4), 248 (100), 210 (21).

Murrayamine H (**3**). Syrup. HRMS: calcd for $C_{24}H_{27}NO_2$, *m/z* 361.2041 $[M]^+$, found 361.2023. UV λ_{max} nm 218, 243, 255, 301, 329. IR ν_{max} cm^{-1}: 3435, 1628, 1580, 1449. EIMS *m/z* (rel. int.): 361 ($[M]^+$, 100), 346 (8), 278 (100), 263 (10), 240 (12)).

Euchrestifoline (**4**). Yellow needles, mp 187–189° (Et_2O). HRMS: calcd for $C_{18}H_{17}NO_2$, *m/z* 279.1258 $[M]^+$, found 279.1215. UV λ_{max} nm (log ε) 231 (4.53), 255 (3.85, sh), 284 (4.15), 291 (4.16), 330 (3.52, sh), 386 (3.80). IR ν_{max} cm^{-1}: 3440, 1650, 1605, 1585, 1490, 1450. EIMS *m/z* (rel. int.): 279 ($[M]^+$, 100), 264 (94), 223 (84), 195 (43), 167 (58), 140 (12), 139 (17), 132 (23)).

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