New Carbazole Alkaloids from *Murraya euchrestifolia*

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Seven new carbazole alkaloids, named pyrayafolines-B (1), -C (3), and -D (5), and euchrestines-A (7), -B (9), -C (10), and -D (11) were isolated from stem bark of *Murraya euchrestifolia* HAYATA (Rutaceae) collected in Taiwan and their structures were characterized by means of spectral methods. Pyrayafoline-B (1) was also synthesized.

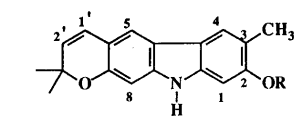
Keywords carbazole alkaloid; *Murraya*; *Murraya euchrestifolia*; Rutaceae; pyrayafoline; euchrestine; NOE

We have isolated many kinds of new carbazole and carbazolequinone alkaloids from *Murraya euchrestifolia* HAYATA (Rutaceae).[1] This paper deals with the isolation and structural elucidation of another seven new monomeric carbazole alkaloids from the stem bark of the same *Murraya* plant collected in Taiwan in May.

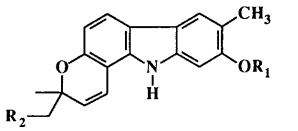
The acetone extract of the stem bark of the plant was subjected successively to silica gel column and preparative thin layer chromatographies (TLC) to give seven new carbazoles named pyrayafolines-B (**1**), -C (**3**), and -D (**5**), each having an alkylated pyran ring in the molecule, and euchrestines-A (**7**), -B (**9**), -C (**10**), and -D (**11**) bearing a terpenoid side chain on the carbazole nucleus.

Results and Discussion

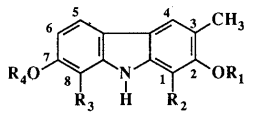
Structure of Pyrayafolines Pyrayafoline-B (**1**) was obtained as a brown powder and found to have the molecular formula $C_{18}H_{17}NO_2$ by high resolution mass (HR-MS) spectrometry. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed a singlet (3H) at δ2.37 due to an aryl methyl, a singlet (6H) at δ1.46 assignable to geminal dimethyls attached to an oxygenated carbon, and AB-type doublets at δ6.48 and 5.58 (each J=9.6 Hz), indicating the presence of a dimethylpyran ring system in the molecule. In the aromatic proton region of the ^{1}H-NMR spectrum, four 1H singlets at δ6.74, 7.62, 7.49, and 6.71 appeared. Among them, the lower field two singlets at δ7.62 and 7.49 were assignable to H-4 and H-5, respectively, which were deshielded by the aromatic ring on the carbazole nucleus.[2] Treatment of this alkaloid with diazomethane in ether–methanol gave a monomethyl ether (**2**), suggesting the presence of a phenolic hydroxy group in the original molecule. In a differential nuclear Overhauser effect (NOE) experiment on the methyl ether (**2**), irradiation of the aryl methyl signal at δ2.34 gave an 8% enhancement of the deshielded H-4 signal at δ7.64. Irradiation of the methoxy signal at δ3.88 caused a 15% increase of the signal at δ6.79 (H-1). On the basis of these



	R
1	H
2	CH_3



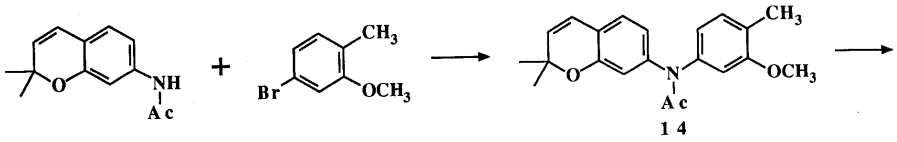
	R_1	R_2
3	H	H
4	CH_3	H
5	H	prenyl
6	CH_3	prenyl



	R_1	R_2	R_3	R_4
7	H	H	prenyl	H
8	H	H	prenyl	CH_3
9	H	H	geranyl	CH_3
10	H	H	geranyl	H
11	H	geranyl	H	H
12	CH_3	geranyl	H	CH_3

prenyl = $-CH_2-CH=C(CH_3)_2$ geranyl = $-CH_2-C(H)=C-CH_2CH_2-CH=C(CH_3)_2$ (CH_3)

Chart 1



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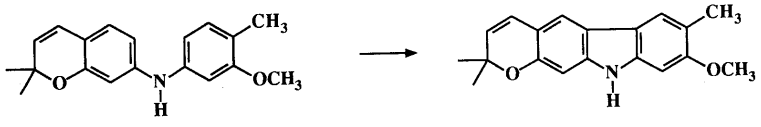

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Chart 2

TABLE I. ^{1}H-NMR Data for Pyrayafolines

	1	2	3	5	6
H-1	6.74 (s)	6.79 (s)	6.82 (s)	6.83 (s)	6.86 (s)
3-CH_3	2.37 (3H, s)	2.34 (3H, s)	2.38 (3H, s)	2.38 (3H, s)	2.34 (3H, s)
H-4	7.62 (s)	7.64 (s)	7.64 (s)	7.64 (s)	7.64 (s)
H-5	7.49 (s)	7.50 (s)	7.63 (d, 8.4)	7.63 (d, 8.4)	7.64 (d, 8.4)
H-6	—	—	6.69 (d, 8.4)	6.68 (d, 8.4)	6.69 (d, 8.4)
H-8	6.71 (s)	6.78 (s)	—	—	—
OH	4.94 (br s)	—	—	4.74 (br s)	—
OCH_3	—	3.88 (3H, s)	—	—	3.90 (3H, s)
NH	7.70 (s)	7.76 (s)	7.78 (s)	7.75 (s)	7.79 (s)
H-1′	6.48 (d, 9.6)	6.49 (d, 9.6)	6.59 (d, 9.8)	6.62 (d, 10.1)	6.63 (d, 10.1)
H-2′	5.58 (d, 9.6)	5.57 (d, 9.6)	5.69 (d, 9.8)	5.66 (d, 10.1)	5.66 (d, 10.1)
H-5′	—	—	—	1.75 (2H, m)	1.75 (2H, m)
H-6′	—	—	—	2.15 (2H, m)	2.15 (2H, m)
H-7′	—	—	—	5.10 (t, 7.1)	5.10 (t, 7.1)
CH_3	1.46 (6H, s)	1.46 (6H, s)	1.47 (6H, s)	1.44 (3H, s)	1.44 (3H, s)
				1.57 (3H, s)	1.57 (3H, s)
				1.65 (3H, s)	1.65 (3H, s)

Values are in δ (ppm). Each signal corresponds to 1H, unless otherwise stated. Figures in parentheses are coupling constants (J) in Hz. s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.

TABLE II. ^{1}H-NMR Data for Euchrestines

	7	8	9	10	11	12
H-1	6.83 (s)	6.82 (s)	6.80 (s)	6.81 (s)	—	—
3-CH_3	2.38 (3H, s)	2.38 (3H, s)	2.38 (3H, s)	2.38 (3H, s)	2.38 (3H, s)	2.44 (3H, s)
H-4	7.65 (s)	7.67 (s)	7.67 (s)	7.65 (s)	7.56 (s)	7.62 (s)
H-5	7.63 (d, 8.4)	7.70 (d, 8.0)	7.70 (d, 8.4)	7.63 (d, 8.4)	7.74 (d, 8.4)	7.82 (d, 8.4)
H-6	6.69 (d, 8.4)	6.82 (d, 8.0)	6.83 (d, 8.4)	6.70 (d, 8.4)	6.68 (dd, 8.4, 2.4)	6.80 (dd, 8.4, 2.4)
H-8	—	—	—	—	6.82 (d, 2.4)	6.87 (d, 2.2)
OH		4.74 (s)	4.75 (s)	—	5.12 (s)	—
OCH_3	—	3.90 (3H, s)	3.90 (3H, s)	—	—	3.88 (3H, s)
						3.78 (3H, s)
NH	7.72 (s)	7.70 (s)	7.73 (s)	7.73 (s)	7.73 (s)	7.82 (s)
H-1′	3.59 (2H, d, 6.7)	3.60 (2H, d, 7.0)	3.62 (2H, d, 6.7)	3.59 (2H, d, 7.1)	3.59 (2H, d, 6.7)	3.68 (2H, d, 7.0)
H-2′	5.36 (t, 6.7)	5.30 (t, 7.0)	5.32 (t, 6.7)	5.37 (t, 6.7)	5.36 (t, 6.7)	5.34 (t, 7.0)
H-5′, H-6′	—	—	2.06 (4H, m)	2.12 (4H, m)	2.11 (4H, m)	2.09 (4H, m)
H-7′	—	—	5.07 (m)	5.07 (m)	5.07 (m)	5.07 (m)
CH_3	1.89 (3H, s)	1.88 (3H, s)	1.87 (3H, s)	1.88 (3H, s)	1.89 (3H, s)	1.91 (3H, s)
	1.78 (3H, s)	1.74 (3H, s)	1.62 (3H, s)	1.65 (3H, s)	1.66 (3H, s)	1.62 (3H, s)
			1.57 (3H, s)	1.58 (3H, s)	1.59 (3H, s)	1.58 (3H, s)

Values are in δ (ppm). Each signal corresponds to 1H, unless otherwise stated. Figures in parentheses are coupling constants (J) in Hz. s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet.

spectral data coupled with the ultraviolet (UV) spectrum (see Experimental), the structure of pyrayafoline-B was proposed to be represented by the formula **1**.

For confirmation of the structure of pyrayafoline-B (**1**), we tried to synthesize this alkaloid. According to our previous paper,[3] the reaction between 7-acetylaminochromene (**13**)[4] and 4-bromo-2-methoxytoluene was carried out in the presence of anhydrous potassium carbonate and copper in pyridine at reflux temperature for 43 h to give **14**. After hydrolysis of the *N*-acetyl group of **14** with KOH in ethanol, treatment of the amine (**15**) with $Pd(OAc)_2$ in dimethylformamide (DMF) for 2 h afforded a cyclization product having a carbazole nucleus. In the ^{1}H-NMR spectrum of this product, observation of two lower field 1H singlets at δ 7.64 and 7.50 assignable to deshielded H-4 and H-5 on the carbazole nucleus, respectively, indicated that cyclization had occurred in the linear direction, as shown by formula **2**. No other conceivable cyclization product could be detected. This synthetic compound **2** was found to be identical with the *O*-methyl ether derived from a natural specimen of pyrayafoline-B by spectrometric comparisons. From these results, the structure of pyrayafoline-B was confirmed to be as shown by formula **1**.

Pyrayafoline-C (**3**) was obtained as a pale yellow oil and found to have the same molecular formula $C_{18}H_{17}NO_2$ as that of pyrayafoline-B (**1**). The ^{1}H-NMR spectrum showed the presence of an aryl methyl, two geminal methyls attached to an oxygenated carbon, a disubstituted double bond, and four aromatic protons as *ortho*-located AB-type doublets and two 1H singlets (Table I). Treatment of this alkaloid with diazomethane gave a monomethyl ether, which was found to be identical with the synthetic specimen of **4** previously reported by us.[3] On the basis of these data, the structure of pyrayafoline-C was proposed to be as shown in formula **3** corresponding to the *O*-desmethyl analogue of pyrayafoline-A (**4**).[5]

Pyrayafoline-D (**5**) was isolated as a pale brown powder, $[\alpha]_D \pm 0°$ (MeOH). The molecular formula was determined as $C_{23}H_{25}NO_2$ by HR-MS. The ^{1}H-NMR spectrum differs from that of pyrayafoline-C (**3**) only in the presence of

signals [δ 1.75 (2H, m), 2.15 (2H, m), 5.10 (1H, t), 1.57 (3H, s), and 1.65 (3H, s)] assignable to the side chain [$-CH_2CH_2CH=C(CH_3)_2$] instead of the signal due to one of the methyls attached to the oxygenated carbon in the spectrum of **3**. The presence of this side chain in the molecule was also indicated by the observation of the characteristic mass fragment base peak at *m/z* 264 [M^+-83] in the MS. Treatment of this alkaloid with diazomethane afforded a monomethyl ether (**6**) as a colorless oil. The MS of the monomethyl ether (**6**) also showed the base fragment at *m/z* 278 corresponding to the loss of [$-CH_2CH_2CH=C(CH_3)_2$] from the molecular ion (*m/z* 361). In the NOE experiments on **6**, irradiation of the aryl methyl signal at δ 2.34 gave an 8% enhancement of the singlet signal at δ 7.64 (H-4). In irradiation of the methoxy signal at δ 3.90, a 15% increase of the singlet signal at δ 6.86 (H-1) was observed. On the basis of the results stated above, we assigned the structure **5** to pyrayafoline-D.

Structure of Euchrestines Euchrestines-A (**7**), -B (**9**), -C (**10**), and -D (**11**) were found to show the following common spectrometric features. 1) These alkaloids revealed analogous UV absorptions having high- and medium-intensity bands at λ_{max} 236—238 and 264—266 nm, respectively, along with twin low-intensity bands at λ_{max} 306—313 and 318—321 nm. These features are characteristic of the 2,7-dioxygenated carbazole chromophore.[6] 2) In the ^{1}H-NMR spectra, each euchrestine showed aromatic proton signals corresponding to four protons. Among them, as common features, lower-field proton signals appearing as a 1H singlet at δ 7.56—7.67 due to H-4, and an *ortho*-coupled 1H doublet at δ 7.63—7.74 (J=8.4 Hz) assignable to H-5, each proton deshielded by the aromatic ring, suggested the absence of substituents at C-4, C-5, and C-6 in the carbazole skeleton. 3) Appearance of a 3H singlet at δ 2.38 in each ^{1}H-NMR spectrum revealed the presence of an aryl methyl group, which was considered likely on biogenetic ground to be located at C-3 on the carbazole nucleus.[2] These results indicated the structure of euchrestines to be 2,7-oxygenated-3-methylcarbazole having a substituent at C-1 or C-8.

Euchrestine-A (**7**) was isolated as a colorless oil and its molecular formula was determined to be $C_{18}H_{19}NO_2$ by HR-MS. Observations of signals at δ 1.89 (3H, s), 1.78 (3H, s), 5.36 (1H, t, J=6.7 Hz), and 3.59 (2H, d, J=6.7 Hz), and a *para*-situated aromatic proton singlet at δ 6.83 besides the common ^{1}H-NMR signals described above indicated the presence of a prenyl group at C-8 of the carbazole nucleus. These spectral data together with the similarity of the ^{1}H-NMR spectrum (Table II) to that of isomurrayafoline-B (**8**) previously reported by us,[6] led us to assign structure **7** to euchrestine-A.

Euchrestine-B (**9**) was obtained as a pale yellow oil. The HR-MS analysis indicated the molecular formula to be $C_{24}H_{29}NO_2$. The presence of a geranyl moiety in the molecule was revealed by observations of proton signals at δ 3.62 (2H, d, J=6.7 Hz), 5.32 (1H, t, J=6.7 Hz), 2.06 (4H, m), 5.07 (1H, m), 1.87 (3H, s), 1.62 (3H, s), and 1.57 (3H, s), the NOE between the methyl group attached to the double bond (δ 1.87) and the benzylic methylene protons (δ 3.62), and a characteristic mass fragment at *m/z* 240 produced by cleavage at the benzylic position. Further, the ^{1}H-NMR spectrum showed a methoxy proton singlet at δ 3.90 and an additional aromatic proton signal at δ 6.80 as a singlet, indicating the location of the geranyl side chain at C-8. In the differential NOE experiment, irradiation of the methoxy signal at δ 3.90 gave a 9% increase of the doublet signal at δ 6.83 due to H-6 suggesting the location of the methoxy group at C-7. On the basis of these results, we proposed the structure **9** for euchrestine-B.

Euchrestine-C (**10**) was obtained as a colorless powder and the molecular formula was determined to be $C_{23}H_{27}NO_2$, different by CH_2 from that of euchrestine-B (**9**), by HR-MS. The presence of a geranyl moiety at C-8, the same as that of euchrestine-B (**9**), was indicated by the ^{1}H-NMR signals (Table II), a mass fragment at *m/z* 266 (M^+-83), and a singlet proton signal at δ 6.81 (H-1). No signal due to an *O*-methyl group was observed. On the basis of these results, euchrestine-C was assigned structure **10**.

Euchrestine-D (**11**) was isolated as a pale yellow oil. The molecular formula, $C_{23}H_{27}NO_2$, was found to be the same as that of euchrestine-C (**10**). The ^{1}H-NMR spectra and MS (Table II and Experimental) of euchrestine-D (**11**) and its *O*,*O*-dimethyl ether (**12**) also showed the presence of a geranyl moiety in the molecule. The appearance of ABC-type signals at δ 7.74 (1H, d, J=8.4 Hz), 6.68 (1H, dd, J=8.4, 2.4 Hz), and 6.82 (1H, d, J=2.4 Hz) assignable to H-5, H-6, and H-8, respectively, in the ^{1}H-NMR spectrum indicated the location of the geranyl moiety at C-1. Treatment of euchrestine-D (**11**) with diazomethane gave the *O*,*O*-dimethyl ether (**12**). In differential NOE experiments on the *O*,*O*-dimethyl ether (**12**), irradiation of the methoxy signal at δ 3.88 gave 2 and 7% increases of the signals at δ 6.80 (H-6) and 6.87 (H-8). On irradiation of another methoxy signal at δ 3.78, a 6% enhancement of the aryl methyl signal at δ 2.44 was seen. Irradiation of the aryl methyl signal at δ 2.44 caused 5 and 6% increases of the signals at δ 3.78 (O–CH_3) and 7.62 (H-4), respectively. Consequently, the structure of euchrestine-D was proposed to be as shown in formula **11**.

Experimental

^{1}H-NMR spectra were recorded on a GX-270 (JEOL) or GX-400 (JEOL) spectrometer in $CDCl_3$. Chemical shifts are shown in δ values (ppm) with tetramethylsilane (TMS) as an internal reference. EI- and HR-MS spectra were taken with an M-80 (Hitachi) spectrometer having a direct inlet system. Infrared (IR) spectra were recorded on a JASCO IR-810 IR spectrophotometer in $CHCl_3$, ultraviolet (UV) spectra on a JASCO UVIDEC-610C double beam spectrophotometer in MeOH, and optical rotation on a DIP-181 polarimeter (JASCO) in $CHCl_3$ at 20 °C. Preparative TLC was carried out with appropriate combinations of $CHCl_3$, hexane, isopropyl ether, benzene, and acetone.

Pyrayafoline-B (1) Brown powder. HR-MS Calcd for $C_{18}H_{17}NO_2$: 279.1258. Found: 279.1266. UV λ_{max} nm: 228, 252, 285, 296 (sh), 329, 353. IR ν_{max} cm^{-1}: 3600, 3470, 3380 (br). ^{1}H-NMR (Table I). EI-MS *m/z* (%): 279 (M^+, 34), 265 (20), 264 (100).

Pyrayafoline-C (3) Pale yellow oil. HR-MS Calcd for $C_{18}H_{17}NO_2$: 279.1258. Found: 279.1258. UV λ_{max} nm: 222, 238, 286 (sh), 296, 323, 351. IR ν_{max} cm^{-1}: 3600, 3470, 3380 (br). ^{1}H-NMR (Table I). EI-MS *m/z* (%): 279 (M^+, 36), 265 (21), 264 (100).

Pyrayafoline-D (5) Pale brown powder, $[\alpha]_D$ 0° (c=0.0013, MeOH). HR-MS Calcd for $C_{23}H_{25}NO_2$: 347.1883. Found: 347.1861. UV λ_{max} nm: 222, 238, 288 (sh), 296, 331, 342. IR ν_{max} cm^{-1}: 3600, 3480, 3380 (br). ^{1}H-NMR (Table I). EI-MS *m/z* (%): 347 (M^+, 22), 265 (19), 264 (100), 263 (12), 234 (6).

Euchrestine-A (7) Colorless oil. HR-MS Calcd for $C_{18}H_{19}NO_2$: 281.1414. Found: 281.1414. UV λ_{max} nm: 213, 236, 265, 295, 313, 318, 329. IR ν_{max} cm^{-1}: 3600, 3470, 3400 (br). ^{1}H-NMR (Table II). EI-MS *m/z* (%): 281 (M^+, 82), 266 (11), 264 (12), 227 (12), 226 (75), 225 (100), 224 (12).

Euchrestine-B (9) Pale yellow oil. HR-MS Calcd for $C_{24}H_{29}NO_2$: 363.2196. Found: 363.2173. UV λ_{max} nm: 212, 238, 264, 310, 318, 331. IR ν_{max} cm^{-1}: 3600, 3470, 3380 (br). ^{1}H-NMR (Table II). EI-MS *m/z* (%): 363 (M^+, 100), 294 (16), 280 (24), 264 (22), 263 (16), 240 (35), 227 (13), 210 (12). Differential NOE: irradiation of 7-OCH_3 (δ 3.90)-9% NOE at H-6 (δ 6.83, 1H, d); irradiation of H-1′ (δ 3.62, 2H, d)-8% NOE at CH_3 (δ 1.87).

Euchrestine-C (10) Colorless powder. HR-MS Calcd for $C_{23}H_{27}NO_2$: 349.2041. Found: 349.2058. UV λ_{max}nm: 212, 237, 266, 306, 320, 329. IR ν_{max} cm^{-1}: 3600, 3470, 3380 (br). ^{1}H-NMR (Table II). EI-MS *m/z* (%): 349 (M^+, 82), 280 (11), 266 (16), 264 (23), 227 (18), 226 (100), 225 (84), 213 (10).

Euchrestine-D (11) Pale yellow oil. HR-MS Calcd for $C_{23}H_{27}NO_2$: 349.2039. Found: 349.2011. UV λ_{max} nm: 212, 238, 265, 312, 321 (sh). IR ν_{max} cm^{-1}: 3600, 3470, 3380 (br). ^{1}H-NMR (Table II). EI-MS *m/z* (%): 349 (M^+, 61), 264 (25), 227 (17), 226 (80), 225 (100), 224 (10), 196 (17).

***O*-Methylation of 1, 3, 5, and 11 with Diazomethane** A large excess of ethereal diazomethane was added to a methanolic solution (20 ml) of **1**, **3**, **5**, or **11** (1—2 mg), and the mixture was left for 2 d at room temperature. The solvent was evaporated off, and the residue was purified by preparative TLC to give almost quantitatively **2**, **4**, **6**, or **12**, respectively. **2**: UV λ_{max} nm: 222, 247, 254, 284, 293, 328, 352. IR ν_{max} cm^{-1}: 3470, 3380 (br). ^{1}H-NMR (Table I). EI-MS *m/z* (%): 293 (M^+, 47), 279 (24), 278 (100), 263 (16). Differential NOE: irradiation of the aryl-CH_3 (δ 2.34)-8% NOE at H-4 (δ 7.64); irradiation of 2-OCH_3 (δ 3.88)-15% NOE at H-1 (δ 6.79). **4**: This product was found to be identical with synthetic pyrayafoline-A (**4**)[3,5] by ^{1}H-NMR and IR comparisons, and co-TLC. **6**: Colorless oil. UV λ_{max} nm: 221, 239, 286 (sh), 295, 333, 338. IR ν_{max} cm^{-1}: 3470, 3380 (br). ^{1}H-NMR (Table I). EI-MS *m/z* (%): 361 (M^+, 35), 279 (20), 278 (100). Differential NOE: irradiation of the aryl-CH_3 (δ 2.34)-8% NOE at H-4 (δ 7.64, 1H, s): irradiation of 2-OCH_3 (δ 3.90)-15% NOE at H-1 (δ 6.86, 1H, s). **12**: UV λ_{max} nm: 212, 238, 262, 305, 315 (sh). ^{1}H-NMR (Table II). EI-MS *m/z* (%): 377 (M^+, 24), 254 (8), 149 (10), 135 (49).

Preparation of *O*-Methylpyrayafoline-B (2) A mixture of 4-bromo-2-methoxytoluene (1.44 g), 7-acetylaminochromene (**13**)[4] (1.0 g), anhydrous K_2CO_3 (650 mg), and Cu (300 mg) in pyridine (2 ml) was refluxed for 43 h. The reaction mixture was diluted with $CHCl_3$, and washed with diluted HCl, and then with H_2O. The $CHCl_3$ solution was dried with anhydrous $MgSO_4$ and evaporated to dryness. The residue was subjected to silica gel chromatography with AcOEt–hexane (1 : 4) to afford **14** (610 mg) as an oil in 39% yield. **14**: HR-MS Calcd for $C_{21}H_{23}NO_3$: 337.1668. Found: 337.1678. IR ν_{max} cm^{-1}: 1660, 1610, 1500. ^{1}H-NMR δ: 7.09 (1H, br d, J=7.4 Hz), 6.94 (1H, d, J=7.4 Hz), 6.70—6.82 (3H, m), 6.65 (1H, s), 6.28 (1H, d, J=9.7 Hz), 5.58 (1H, d, J=9.7 Hz), 3.79 (3H, s), 2.19 (3H, s), 2.07 (3H, s), 1.41 (6H, s). EI-MS *m/z*: 337 (M^+), 323, 322, 280, 162, 161.

After treatment of **14** (380 mg) with 20% KOH–EtOH (20 ml) at reflux temperature for 1.5 h, the solvent was evaporated off and the residue was diluted with H_2O, then extracted with $CHCl_3$. The $CHCl_3$ extract was washed with H_2O and dried with anhydrous $MgSO_4$, and then the solvent was evaporated off to give **15** as an oil in 99% yield. **15**: HR-MS Calcd for $C_{19}H_{21}NO_2$: 295.1571. Found: 295.1561. IR ν_{max} cm^{-1}: 3430, 1610, 1570, 1510. ^{1}H-NMR δ: 7.02 (1H, br), 7.02 (1H, d, J=7.4 Hz), 6.83 (1H, d, J=7.4 Hz), 6.62 (1H, d, J=7.4 Hz), 6.60 (1H, s), 6.48 (1H, d, J=7.4 Hz), 6.46 (1H, s), 6.26 (1H, d, J=9.7 Hz), 5.44 (1H, d, J=9.7 Hz), 3.78 (3H, s), 2.16 (3H, s), 1.41 (6H, s). EI-MS *m/z*: 295, 281, 280 (100%), 265, 236, 144, 140. A solution of **15** (25 mg) in DMF (20 ml) was refluxed in the presence of $Pd(OAc)_2$ (20 mg) under argon gas for 2 h. The solvent was evaporated off and the residue was diluted with H_2O, and then extracted with AcOEt. The AcOEt extract was dried with anhydrous $MgSO_4$ and the solvent was evaporated off. The residue was subjected to preparative silica gel TLC to give **2** (2 mg, 9% yield) as a pale yellow oil, which was found to be identical with a natural specimen of *O*-methylpyrayafoline-B by NMR and IR comparisons, and co-TLC.

References and Notes

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5) Pyrayafoline (**4**) reported previously[3] will be renamed pyrayafoline-A (**4**).

6) C. Ito, T.-S. Wu, and H. Furukawa, *Chem. Pharm. Bull.*, **35**, 450 (1987) and our unpublished data.