Novel Binary Carbazole Alkaloids from *Murraya euchrestifolia*[1)]

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Seven new binary carbazole alkaloids, named murrastifoline-A (1), -B (2), -C (3), and -D (4) and chrestifoline-A (5), -B (6), and -C (7), were isolated from root bark of *Murraya euchrestifolia* HAYATA (Rutaceae) collected in Taiwan and their structures were elucidated by means of spectral methods.

Keywords carbazole alkaloid; binary; dimer; *Murraya euchrestifolia*; Rutaceae; murrastifoline; chrestifoline

As a part of a continuing phytochemical investigation of chemical constituents of *Murraya* plants,[2-4)] we have so far isolated nine binary carbazole alkaloids as well as various monomeric carbazoles and carbazolequinones from *M. euchrestifolia* HAYATA and characterized them.[3,4)] This paper deals with the isolation and structural elucidation of another seven new binary carbazole alkaloids from the root bark of the same *Murraya* plant collected in Taiwan in February, 1980.[4)]

The acetone extract of the root bark was subjected successively to silica gel column and preparative thin-layer chromatographies (TLC) as reported previously[4)] to give seven binary carbazoles named murrastifoline-A (**1**), -B (**2**), -C (**3**), and -D (**4**) and chrestifoline-A (**5**), -B (**6**), and -C (**7**).

Results and Discussion

Structure of Murrastifolines Initially, the presence of the *N*-substituted 1-methoxy-3-methylcarbazole system (A) as a common structural unit in the four murrastifolines (**1**, **2**, **3**, and **4**) was suggested by the following spectral data. (a) In the ultraviolet (UV) spectrum, each alkaloid showed sharp absorptions at λ_{max} 238—243 nm and at λ_{max} 287—292 nm, and a broad band at λ_{max} 325—350 nm with strong, medium, and weak intensities, respectively.[5)] (b) In the studies of the proton nuclear magnetic resonance (^{1}H-NMR) spectra (Table I) using proton–proton correlation spectroscopy (H–H COSY), each compound showed two 3H singlets at δ 3.57—4.11 and at δ 2.52—2.56 due to a methoxy and an aryl methyl group, respectively, two 1H singlets at δ 6.85—7.00 and at δ 7.56—7.63, the lower characteristic of H-4 in the carbazole nucleus, and signals of a four-spin proton system at δ 7.88—8.13 (doublet, J=7.9 Hz), 7.12—7.21 (triplet, J=7.9 Hz), 7.29—7.34 (triplet, J=7.9 Hz), and 7.16—7.46 (doublet, J=7.9 Hz) assignable to H-5, H-6, H-7, and H-8, respectively. (c) Observations of nuclear Overhauser effect (NOE) enhancements between an aryl methyl signal and two 1H singlets, and between a methoxy signal and a higher-field singlet at δ 6.85—7.00 (see Experimental) suggested the location of the aryl methyl and methoxy group at C-3 and C-1, respectively. (d) The appearance of a mass fragment peak at *m/z* 210 or 211 corresponding to an ion of formula $C_{14}H_{12-13}NO$ supported the presence of the structural unit A in each murrastifoline molecule. The structure of another carbazolemoiety of each molecule will be discussed below.

Structure of Murrastifoline-A (1) Murrastifoline-A (**1**) was obtained as a colorless oil and the molecular formula was determined as $C_{28}H_{24}N_2O_2$ by high resolution mass spectrometry (HR-MS). In the ^{1}H-NMR spectrum, except for the signals due to protons of the common structural unit (A), two 3H singlets at δ 2.48 and 4.03, and two 1H singlets at δ 7.54 and 6.88 were observed. On the basis of differential NOE experiments (see Experimental), these signals were assigned to 3′-methyl, 1′-methoxy, H-4′, and H-2′ protons, respectively, in the carbazole nucleus. The remaining signals were a broad singlet at δ 10.45 (NH) and an ABC-type feature at δ 8.10 (1H, d, J=2.0 Hz), 7.40 (1H, dd, J=2.0 and 7.9 Hz), and 7.67 (1H, d, J=7.9 Hz). Since the lowest doublet at δ 8.10 was characteristic of deshielded H-5′ in the carbazole nucleus, the location of the linkage to the nitrogen of the common carbazole unit (A) was determined at C-6′. From these spectral results, the structure of murrastifoline-A was proposed as formula **1**, corresponding to a dimer of murrayafoline-A[4)] co-occurring in the same plant.

Structure of Murrastifoline-B (2) Murrastifoline-B (**2**) was isolated as a colorless oil having the molecular formula $C_{27}H_{22}N_2O_2$, a difference of CH_2 compared with **1**. The appearance of two sets of four spin systems in the ^{1}H-NMR spectrum (Table I) revealed the presence of a non-substituted ring in another carbazole nucleus. Two 1H doublets at δ 7.81 and 7.04 (J=1.5 Hz) were found to be *meta*-coupled to each other and the lower-field doublet at δ 7.81 was assignable to deshielded H-4′ in the carbazole nucleus. Further, irradiation of the methoxy signal at δ 4.03 gave an NOE enhancement of the signal at δ 7.04 (H-2′). These results led us to the structure **2** for murrastifoline-B.

Structure of Murrastifoline-C (3) Murrastifoline-C (**3**), a colorless oil, $[\alpha]_D$ 0° (chloroform), was found to have the

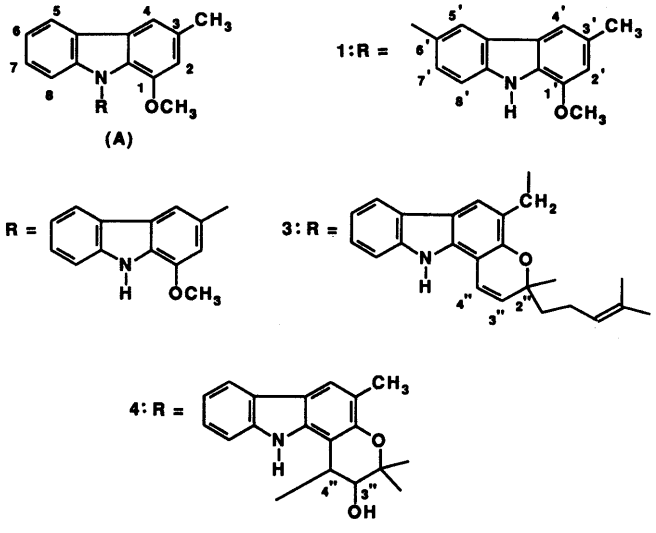


TABLE I. ^{1}H-NMR Data for Murrastifolines and Chrestifolines

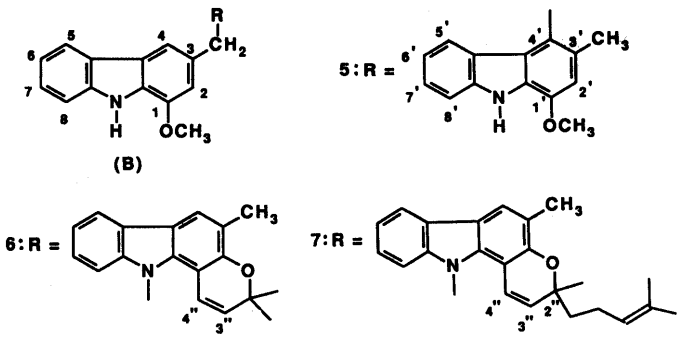
	1-OCH_3 1′-OCH_3 (3H)	H-2 H-2′	3-CH_3 3′-CH_3 (3H)	3-CH_2 (2H)	H-4 H-4′	H-5 H-5′	H-6 H-6′	H-7 H-7′	H-8 H-8′	N-H	Others
1	3.57 s	6.85 s	2.52 s	—	7.63 s	8.13 d (7.9)	7.21 t (7.9)	7.33 t (7.9)	7.16 d (7.9)	—	
	4.03 s	6.88 s	2.48 s	—	7.54 s	8.10 d (2.0)	—	7.40 dd (7.9, 2.0)	7.67 d (7.9)	10.45 s	
2	3.61 s	6.86 s	2.52 s	—	7.63 s	(8.13 d (7.9)	7.20 t (7.9)	7.34 t (7.9)	7.22 d (7.9))	—	
	4.03 s	7.04 d (1.5)	—	—	7.81 d (1.5)	8.13 d (7.9))	7.21 t (7.9)	7.44 t (7.9)	7.65 d (7.9))	10.59 s	
3	3.95 s	6.90 s	2.51 s	—	7.58 s	(8.07 d (7.9)	7.12 t (7.9)	7.29 t (7.9)	7.46 d (7.9))	—	
	—	—	—	6.03 s	7.36 s	7.59 d (7.9))	6.99 t (7.9)	7.20 t (7.9)	7.35 d (7.9))	10.33 s	6.96 d (9.9), 5.77 d (9.9), 1.38 s (3H), 1.70 m (2H), 2.08 m (2H), 5.14 t (7.3), 1.67 s (3H), 1.59 s (3H)
4	4.11 s	7.00 s	2.56 s	—	7.56 s	(7.88 d (7.9)	6.92 t (7.9)		6.75 d (7.9))		
	—	—	2.43 s	—	7.87 s	7.98 d (7.9))	6.94 t (7.9)	6.95—7.05 (3H, overlapped)		8.53 s	7.21 d (9.2), 4.48 d (5.9), 4.38 dd (5.9, 9.2), 1.55 s (3H), 1.42 s (3H)
5	3.84 s	7.00 s	—	4.78 s	7.39 s	7.78 d (7.9)	7.03 t (7.9)	7.28 t (7.9)	7.49 d (7.9)	(10.16 s	
	4.02 s	6.94 s	2.47 s	—	—	8.08 d (7.9)	6.98 t (7.9)	7.27 t (7.9)	7.55 d (7.9)	10.28 s)	
6	3.85 s	6.90 s	—	5.79 s	7.38 s	7.77 d (7.9)	7.01 t (7.9)	7.28 t (7.9)	7.48 d (7.9)	10.31 s	
	—	—	2.27 s	—	7.81 s	7.99 d (7.9)	7.13 t (7.9)	7.26 t (7.9)	7.39 d (7.9)	—	6.91 d (9.9), 5.53 d (9.9), 1.36 s (6H)
7	3.85 s	6.90 s	—	5.80 s	7.38 s	7.77 d (7.9)	7.01 t (7.9)	7.28 t (7.9)	7.48 d (7.9)	10.31 s	
	—	—	2.30 s		7.81 s	7.98 d (7.9)	7.12 t (7.9)	7.26 t (7.9)	7.38 d (7.9)	—	6.95 d (9.9), 5.53 d (9.9), 1.34 s (3H), 1.68 m (2H), 2.04 m (2H), 5.00 t (7.3), 1.54 s (3H), 1.45 s (3H)

Values are in δ (ppm). Figures in parentheses are coupling constants in Hz. Each signal corresponds to 1H, unless otherwise stated. s, singlet; d, doublet; t, triplet; dd, double doublet; m, multiplet. Recorded in acetone-d_6.

molecular formula $C_{37}H_{36}N_2O_2$ from the HR-MS. In the EI-MS, this alkaloid showed the base fragment peak at *m/z* 330 as well as the fragment at *m/z* 211 due to A. The H–H COSY spectrum in acetone-d_6 showed the presence of two sets of four spin proton systems in the aromatic proton region, indicating the lack of substituents in one ring of both carbazole skeletons. Further, in the ^{1}H-NMR spectrum, the AB-type doublets (J=9.9 Hz) at δ 6.96 and 5.77 and a 3H singlet at δ 1.38 were ascribed to protons of a double bond and an oxygen-linked tertiary methyl in a pyran ring system, and signals at δ 5.14 (1H, t, J=7.3 Hz), 2.08 (2H, m), 1.70 (2H, m), 1.67 (3H, s), and 1.59 (3H, s) were assigned to protons of a [–CH_2CH_2–CH=$C(CH_3)_2$] side chain attached to an oxygen-linked quaternary carbon atom. The presence of this side chain was also supported by the observation of a mass fragment at *m/z* 457 corresponding to the ion [M^+ – ·CH_2CH_2–CH=$C(CH_3)_2$]. The H–H COSY and nuclear Overhauser enhancement and exchange spectroscopy (NOESY) showed a correlation between a 1H broad singlet at δ 7.36 (deshielded H-4′) and a 2H singlet at δ 6.03 which was assigned to benzylic methylene protons linked to a nitrogen in A. Based on these results, we assigned the structure **3** to murrastifoline-C.

Structure of Murrastifoline-D (4) Murrastifoline-D (**4**), $C_{32}H_{30}N_2O_3$, was obtained as a colorless oil, $[\alpha]_D$ 0° (chloroform). The EI-MS showed a base fragment peak at *m/z* 280 together with a fragment at *m/z* 211 corresponding to the ion [A + ·H]$^+$. The appearance of geminal dimethyl signals at δ 1.55 and 1.42 and a double doublet (J=5.9 and 9.2 Hz) at δ 4.38 coupled with a hydroxy proton at δ 4.48 (1H, d, J=5.9 Hz, disappeared with D_2O) and a signal at δ 7.21 (1H, d, J=9.2 Hz) assigned to H-4″ attached to a benzylic carbon directly bonded to a nitrogen of A, indicated the presence of a 2,2-dimethyl-3-hydroxy-4-substituted dihydropyran ring system. The J value (9.2 Hz) of the AB-type protons and the absence of NOE between these two protons suggested the *trans* relationship of the substituents at C-3″ and C-4″. In the aromatic proton region, two lower-field doublets (δ 7.98 and 7.88, J= 7.9 Hz) and two lower singlets (δ 7.87 and 7.56) were characteristic of protons at C-5 and C-4 on two carbazole nuclei. The observation of a doublet at δ 6.75 (1H, J= 7.9 Hz), two triplets at δ 6.92 and 6.94 (each 1H, J=7.9 Hz) and overlapped 3H signals together with two lower doublets at δ 7.88 and 7.98 described above suggested a lack of substituents in one ring of both carbazole skeletons. According to these observations, murrastifoline-D can be represented by the structure **4**.

Structure of Chrestifolines The UV absorptions having sharp bands at λ_{max} 241—243 (strong) and 290—291 nm (medium), and broad and weak bands at λ_{max} 326—330 and 340—342 nm in the spectra of chrestifoline-A (**5**), -B (**6**), and -C (**7**) were suggestive of the presence of the carbazole chromophore. In each ^{1}H-NMR spectrum using an H–H COSY technique, the appearance of two sets of four spin systems in the aromatic proton region as shown in Table I indicated that one of the rings on each carbazole nucleus was unsubstituted. Further, the ^{1}H-NMR spectrum of each alkaloid revealed a 3H singlet at δ 3.84 or 3.85 (OCH_3), two 1H-singlets at δ 7.00 or 6.90 and 7.39 or 7.38, a lower singlet assignable to a deshielded H-4, and a 2H singlet at δ 4.78—5.80 ascribed to the benzylic methylene protons bonded to a nitrogen or sp^2-carbon in another carbazole nucleus. In NOE experiments on the chrestifolines, irradiation of a methoxy signal gave an enhancement of the signal of the higher singlet at δ 7.00 or 6.90. On irradiation of the benzylic methylene signal, both singlet signals in the aromatic proton region showed area increases. From the



results of these spectral data as well as the appearance of a mass fragment peak at m/z 210, each chrestifoline was found to have a 1-methoxy-3-(substituted methylene)carbazole nucleus (B) as a common structural unit. Therefore, the structural establishment of each chrestifoline (**5**, **6**, and **7**) requires determination of the substitution pattern in the other carbazole skeleton.

Structure of Chrestifoline-A (5) Chrestifoline-A (**5**) was obtained as a colorless oil and the molecular formula was established as $C_{28}H_{24}N_2O_2$ by HR-MS. The EI-MS showed a molecular ion at m/z 420 as a base peak and a fragment peak at m/z 210 which was due to a half of the molecule. In the ^{1}H-NMR spectrum, except for signals due to a common unit B and another non-substituted ring, a methoxy signal at δ 4.02, an aryl methyl signal at δ 2.47, an aromatic 1H singlet at δ 6.94, and an N-H proton signal at 10.28 (or 10.16) were observed. In NOE experiments, irradiation of the methoxy signal at δ 4.02 caused an enhancement of the signal at δ 6.94 (H-2′), and irradiation of the aryl methyl signal at δ 2.47 caused area increases of the signals at δ 6.94 (H-2′) and δ 4.78 (benzylic methylene). Conversely, irradiation of the benzylic methylene signal at δ 4.78 enhanced the signals at δ 2.47 (aryl methyl) and δ 8.08 (H-5′), except for signals due to B. These results led us to assign the structure of chrestifoline-A as formula **5**.

Structure of Chrestifoline-B (6) Chrestifoline-B (**6**), a colorless oil, was found to have the molecular formula $C_{32}H_{28}N_2O_2$. The EI-MS showed fragment peaks at m/z 263 and 248 together with a molecular ion (m/z 472) and a base peak at m/z 210 due to the partial structural unit B. In the ^{1}H-NMR spectrum, an aryl methyl signal at δ 2.27, a deshielded H-4′ signal at δ 7.81, and signals due to a dimethylpyran ring at δ 1.36 (6H, s), 6.91 (1H, d, J=9.9 Hz), and 5.53 (1H, d, J=9.9 Hz) were observed. In NOE experiments, irradiation of the aryl methyl signal at δ 2.27 caused an area increase of the signal at δ 7.81 (H-4′). On irradiation of the benzylic methylene signal at δ 5.79, enhancements of signals at δ 6.91 (H-4″), 6.90 (H-2), 7.39 (H-8′), and 7.38 (H-4) were observed. On the basis of these data, including the lower chemical shift of the benzylic methylene proton (δ 5.79), the structure of chrestifoline-B was proposed as formula **6**.

Structure of Chrestifoline-C (7) Chrestifoline-C (**7**) was isolated as a colorless oil, $[\alpha]_D$ −5.6° (chloroform), $C_{37}H_{36}N_2O_2$. The ^{1}H-NMR spectrum of chrestifoline-C showed signals assignable to a deshielded H-4′ (δ 7.81) an aryl methyl (δ 2.30), a methyl (δ 1.34) attached to a quaternary carbon bearing an oxygen, and a double bond in a pyran ring [δ 6.95 and 5.53 (each 1H, d, J=9.9 Hz)], besides signals due to protons on B and a non-substituted ring in another carbazole nucleus. The presence of a side chain of [(–O–C–)$CH_2CH_2CH=C(CH_3)_2$] in the molecule was suggested from the observation of signals at δ 5.00 (1H, t, J=7.3 Hz), 2.04 (2H, m), 1.68 (2H, m), 1.54 (3H, s), and 1.45 (3H, s) in the ^{1}H-NMR spectrum, and the appearance of mass fragments at m/z 457 and 248 corresponding to loss of 83 mass units, corresponding to [$CH_2CH_2CH=C(CH_3)_2$], from the molecular ion and from the other half (m/z 331) of the molecule, respectively. In NOE experiments, irradiation of the aryl methyl signal at δ 2.30 revealed an enhancement of the signal at δ 7.81 (H-4′), and irradiation of the benzylic methylene proton at δ 5.80 caused enhancements of the signal at δ 6.95 (H-4″) and 7.38 (H-8′) as well as signals at δ 7.38 (H-4) and 6.90 (H-2) on B. These results led us to propose the structure **7** for chrestifoline-C, except for the absolute stereochemistry.

Experimental

IR spectra were recorded on a Jasco IR-810 infrared spectrophotometer in $CHCl_3$, UV spectra on a Jasco UVIDEC-610C double beam spectrophotometer in MeOH, optical rotations on DIP-181 (JASCO) in $CHCl_3$, and ^{1}H-NMR spectra on a JEOL GX-400 NMR spectrometer (with $SiMe_4$ as an internal standard) in acetone-d_6. EI- and HR-MS were measured on a Hitachi M-52, Hitachi M-80 or JMS-HX-110 mass spectrometer. NOE enhancements were determined by differential NOE or NOESY, and all COSY spectra were recorded on a JEOL GX-400 spectrometer. All TLC procedures and preparative TLC were done on Kieselgel 60 F_{254} (Merck).

Isolation of Murrastifolines and Chrestifolines The acetone extract (14 g) of root bark of *Murraya euchrestifolia* HAYATA collected in Taiwan on February, 1980[4] was subjected successively to silica gel column chromatography and preparative TLC (developed with an appropriate mixture of benzene, acetone, isopropyl ether, hexane, $CHCl_3$, and CH_2Cl_2) to give murrastifoline-A (**1**) 2 mg (0.0006% from dried root bark), -B (**2**) 2 mg (0.0006), -C (**3**) 2 mg (0.0006), and -D (**4**) 2 mg (0.0006) and chrestifoline-A (**5**) 11 mg (0.0033), -B (**6**) 8 mg (0.0024), and -C (**7**) 6 mg (0.0018) as well as monomeric and other binary carbazoles.[4]

Murrastifoline-A (1) Colorless oil. UV λ_{max} nm: 227, 243, 285, 291, 334, 347. IR ν_{max}: 3470 cm^{-1}. EI-MS m/z (%): 420 (M^+, 100), 389 (19), 373 (13), 211 (4), 210 (16). HR-MS: Calcd for $C_{28}H_{24}N_2O_2$: 420.1835. Found: 420.1800; Calcd for $C_{14}H_{12}NO$: 210.0918. Found: 210.0920. NOE: Irradiation at δ 2.52 (3-CH_3): enhancements at δ 7.63 (H-4, 7%), 6.85 (H-2, 9%); irradiation at δ 3.57 (1-OCH_3): enhancement at δ 6.85 (H-2, 15%); irradiation at δ 2.48 (3′-CH_3): enhancements at δ 7.54 (H-4′, 6%), 6.88 (H-2′, 7%); irradiation at δ 4.03 (1′-OCH_3): enhancement at δ 6.88 (H-2′, 16%).

Murrastifoline-B (2) Colorless oil. UV λ_{max} nm: 226, 242, 252, 280, 292, 335. IR ν_{max}: 3470 cm^{-1}. EI-MS m/z (%): 406 (M^+, 100), 360 (41), 211 (4), 210 (9), 203 (13), 196 (6). HR-MS: Calcd for $C_{27}H_{22}N_2O_2$: 406.1679. Found: 406.1658; Calcd for $C_{14}H_{12}NO$: 210.0918. Found: 210.0966. NOE: Irradiation at δ 2.52 (3-CH_3): enhancements at δ 7.63 (H-4, 6%) and 6.86 (H-2, 10%); irradiation at δ 3.61 (1-OCH_3): enhancement at δ 6.86 (H-2, 12%); irradiation at δ 4.03 (1′-OCH_3): enhancement at δ 7.04 (H-2′, 15%).

Murrastifoline-C (3) Colorless oil, $[\alpha]_D$ 0° (c=0.10, $CHCl_3$). UV λ_{max} nm: 205, 238, 254, 263, 287, 335, 353. IR ν_{max}: 3470 cm^{-1}. EI-MS m/z (%): 540 (M^+, 28), 457 (9), 330 (100), 211 (78), 210 (16), 196 (50). HR-MS: Calcd for $C_{37}H_{36}N_2O_2$: 540.2774. Found: 540.2773; Calcd for $C_{14}H_{13}NO$: 211.0996. Found: 211.1003. NOESY: Correlation between δ 3.95 (1-OCH_3), 6.90 (H-2); δ 2.51 (3-CH_3), 7.58 (H-4), 6.90 (H-2); δ 6.03 (3′-CH_2), 7.36 (H-4′).

Murrastifoline-D (4) Colorless oil, $[\alpha]_D$ 0° (c=0.057, $CHCl_3$). UV λ_{max} nm: 205, 230, 239, 254 (sh), 292, 302, 332, 347. IR ν_{max}: 3460 cm^{-1}. EI-MS m/z (%): 490 (M^+, 35), 280 (100), 279 (46), 238 (27), 222 (19), 211 (62), 210 (34). HR-MS: Calcd for $C_{32}H_{30}N_2O_3$: 490.2254. Found: 490.2227; Calcd for $C_{14}H_{13}NO$: 211.0996. Found: 211.1016. NOE: Irradiation at δ 4.11 (1-OCH_3): enhancement at δ 7.00 (H-2, 17%); irradiation at δ 2.56 (3-CH_3): enhancements at δ 7.56 (H-4, 9%), 7.00 (H-2, 24%); irradiation at δ 2.43 (3′-CH_3): enhancement at δ 7.87 (H-4′, 13%).

Chrestifoline-A (5) Colorless oil. UV λ_{max} nm: 225, 243, 252 (sh). 282, 291, 330, 342. IR ν_{max}: 3470 cm^{-1}. EI-MS m/z (%): 420 (M^+, 100), 405 (47), 273 (84), 211 (41), 210 (47). HR-MS: Calcd for $C_{28}H_{24}N_2O_2$: 420.

1836. Found: 420.1804; Calcd for $C_{14}H_{12}NO$: 210.0919. Found: 210.0920. NOE: Irradiation at δ 4.02 (1'-OCH_3): enhancement at δ 6.94 (H-2', 15%); irradiation at δ 2.47 (3'-CH_3): enhancements at δ 6.94 (H-2', 9%), 4.78 (3-CH_2, 6%); irradiation at δ 3.84 (1-OCH_3): enhancement at δ 7.00 (H-2, 18%); irradiation at δ 4.78 (3-CH_2): enhancements at δ 7.00 (H-2, 10%), 7.39 (H-4, 6%), 2.47 (3'-CH_3, 10%), 8.08 (H-5', 18%).

Chrestifoline-B (6) Colorless oil. UV λ_{max} nm: 226, 241, 252, 260 (sh), 280, 290, 326, 340, 360. IR ν_{max}: 3470 cm^{-1}. EI-MS *m/z* (%): 472 (M^+, 18), 263 (31), 248 (27), 211 (19), 210 (100). HR-MS: Calcd for $C_{32}H_{28}N_2O_2$: 472.2148. Found: 472.2134. Calcd for $C_{14}H_{12}NO$: 210.0917. Found: 210.0883. NOE: Irradiation at δ 2.27 (3'-CH_3): enhancement at δ 7.81 (H-4', 8%); irradiation at δ 3.85 (1-OCH_3): enhancement at δ 6.90 (H-2, 13%); irradiation at δ 5.79 (3-CH_2): enhancements at δ 7.38 and 7.39 (H-4 and 8', total 17%), 6.90 and 6.91 (H-2 and 4'', total 24%).

Chrestifoline-C (7) Colorless oil. $[\alpha]_D$ $-5.6°$ (c=0.054, $CHCl_3$). UV λ_{max} nm: 226, 242, 251, 282, 290, 327, 341, 360. IR λ_{max}: 3470 cm^{-1}. EI-MS *m/z* (%): 540 (M^+, 22), 457 (30), 331 (22), 248 (70), 211 (18), 210 (100). HR-MS: Calcd for $C_{37}H_{36}N_2O_2$: 540.2774. Found: 540.2774; Calcd for $C_{14}H_{12}NO$: 210.0917. Found: 210.0900. NOE: Irradiation at δ 2.30 (3'-CH_3): enhancement at δ 7.81 (H-4', 12%); irradiation at δ 3.85 (1-OCH_3): enhancement at δ 6.90 (H-2, 12%); irradiation at δ 5.80 (3-CH_2): enhancements at δ 6.90 (H-2, 9%), 7.38 and 7.38 (H-4 and 8', total 20%), 6.95 (H-4'', 18%).

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