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Studies on the Alkaloids from *Picrasma quassioides* BENNET. IV.[1] Structures of Picrasidines I, J, and K

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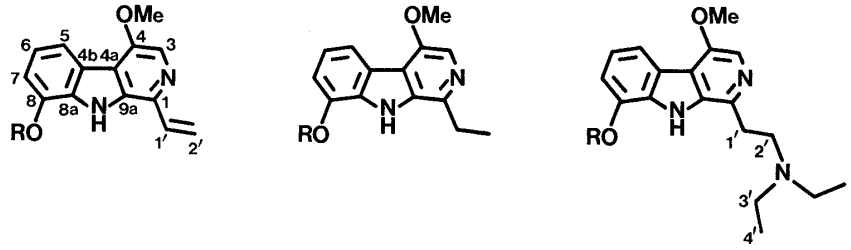
Three new β-carboline alkaloids, picrasidines I (I), J (II), and K (III), were isolated from the bark of *Picrasma quassioides* BENNET. The structures were determined on the basis of spectral analyses and chemical transformations.

Keywords——*Picrasma quassioides*; Simaroubaceae; bark; picrasidine I; picrasidine J; picrasidine K; β-carboline alkaloid

In earlier studies on the alkaloids from *Picrasma quassioides* BENNET (Simaroubaceae, Japanese name "Nigaki") grown in Japan, we isolated several new β-carboline alkaloids.[1-3] This paper deals with the structural elucidation of three new β-carboline alkaloids, picrasidines I (I), J (II), and K (III), isolated from the bark of the plant.



I: R=H IV: R=Ac VII: R=Me

II: R=H V: R=Ac VIII: R=Me

III: R=H VI: R=Ac IX: R=Me

Chart 1

Picrasidines I (I), J (II), and K (III) each showed an orange color on reaction with Dragendorff's reagent and were determined to have the molecular formulae $C_{14}H_{12}N_2O_2$, $C_{14}H_{14}N_2O_2$, and $C_{18}H_{23}N_3O_2$, respectively, by high-resolution mass spectrometry. The striking similarity of the ultraviolet (UV) absorptions among picrasidines I (I), J (II), and K (III) suggested that they possess the same basic β-carboline structure.[1-3] The UV bands showed a bathochromic shift upon addition of 0.02 N sodium hydroxide solution and 0.02 N hydrochloric acid solution, indicating the presence of phenolic OH and NH of the β-carboline structure. The infrared (IR) absorptions at 3420 and 3320 cm^{-1} for I, at 3450 and 3140 cm^{-1} for II, and at 3470 and 3120 cm^{-1} for III were assigned to the NH and OH groups, respectively. The presence of at least one phenolic hydroxyl group in each molecule was confirmed by the appearance of a deep green color on reaction with ferric chloride and by acetylation to give 8-*O*-monoacetylpicrasidines I (IV), J (V), and K (VI). The proton magnetic resonance (^{1}H-NMR) spectra of the three alkaloids in deuteriodimethyl sulfoxide (DMSO-d_6)

were also similar, and the two lowest field singlets [δ 10.03 and 11.53 for I, 9.95 and 11.33 for II, and 10.02 and 11.72 for III (each 1H, s and each exchangeable on deuteration)] were assigned to the phenolic OH proton and the NH proton of the indole moiety, respectively, and isolated ABX pattern signals [δ 7.65 (1H, dd, J=7.7 and 1.0 Hz), 7.06 (1H, t, J=7.7 Hz), and 6.95 (1H, dd, J=7.7 and 1.0 Hz) for I, 7.63 (1H, dd, J=7.7 and 1.0 Hz), 7.02 (1H, t, J=7.7 Hz), and 6.91 (1H, dd, J=7.7 and 1.0 Hz) for II, and 7.64 (1H, dd, J=7.8 and 1.0 Hz), 7.02 (1H, t, J=7.8 Hz), and 6.92 (1H, dd, J=7.8 and 1.0 Hz) for III] were assigned to 5-H to 7-H. Two proton singlets [δ 4.11 (3H, s) and 8.07 (1H, s) for I, 4.05 (3H, s) and 7.91 (1H, s) for II, and 4.06 (3H, s) and 7.91 (1H, s) for III] were assigned to the methoxyl group and the lone aromatic proton (3-H), respectively. In order to determine the location of the methoxyl and hydroxyl groups, a nuclear Overhauser effect (NOE) experiment was carried out on I, II, and III. Irradiation of the methoxyl signals of I at δ 4.11, II at δ 4.05, and III at δ 4.06 produced 23%, 21%, and 18% enhancements of the 3-H signals at δ 8.07, 7.91, and 7.91, respectively. Therefore, in all three compounds, the methoxyl groups were unambiguously placed at C-4 and the hydroxyl group at C-8; this was supported by a deep coloration on reaction with Gibbs' reagent. The major differences among I, II, and III were in the spectral features arising from the C-1 functional group. In picrasidine I, AMX pattern signals at δ 5.40, 6.30, and 7.61 (J_{AM}=16.9 Hz, J_{AX}=10.6 Hz, and J_{MX}=2.2 Hz) were observed and assigned to a vinyl group. In picrasidine J, A_2B_3 pattern signals at δ 1.30 (3H, t, J=7.7 Hz) and 3.10 (2H, q, J=7.7 Hz) were observed and assigned to an ethyl group. Methylation of picrasidines I and J was carried out with diazomethane to afford 8-*O*-methylpicrasidine I (VII) and 8-*O*-methylpicrasidine J (VIII), respectively. Since the structures of these compounds (VII and VIII) were unequivocally determined by us,[2-3] the structures of picrasidines I and J were proposed to be I and II, respectively. In the case of picrasidine K, A_2B_3 pattern signals at δ 1.00 (6H, t, J=7.1 Hz) and 2.61 (4H, q, J=7.1 Hz) were observed and assigned to two equivalent ethyl groups, and A_2B_2 pattern signals at δ 3.22 and 3.87 (each 2H, t, J=7.3 Hz) to a 1,2-disubstituted ethane grouping. These spin-systems were not spin–spin coupled with each other. Substraction of the β-carboline formula $C_{12}H_9N_2O_2$ from the molecular formula gave a partial formula $C_6H_{14}N$. On the basis of these results, picrasidine K has a $-CH_2CH_2-\overset{+}{N}=(C_2H_5)_2$ grouping at the C-1 position. The mass spectrum (MS) of picrasidine K showed significant fragment ion peaks at m/z 86 [base ion, $H_2C-\overset{+}{N}=(C_2H_5)_2$ by cleavage of the C(1′)–C(2′) bond] and m/z 58 [$CH_2=\overset{+}{N}H-C_2H_5$ by cleavage of the C(2′)–N bond $-CH_2$]. On the basis of the above data, picrasidine

TABLE I. ^{1}H-NMR Spectral Data for Compounds I, II, and III

Proton	I	II	III
H-3	8.07 (s)	7.91 (s)	7.91 (s)
H-5	7.65 (dd, J=7.7, 1.0 Hz)	7.63 (dd, J=7.7, 1.0 Hz)	7.64 (dd, J=7.8, 1.0 Hz)
H-6	7.06 (t, J=7.7 Hz)	7.02 (t, J=7.7 Hz)	7.02 (t, J=7.8 Hz)
H-7	6.95 (dd, J=7.7, 1.0 Hz)	6.91 (dd, J=7.7, 1.0 Hz)	6.92 (dd, J=7.8, 1.0 Hz)
NH	11.53 (s)[a]	11.33 (s)[a]	11.72 (s)[a]
H_M H_A / $C=C$ / H_A H_X H_M H_X	7.61 [J_{AM}=16.9 Hz] / 6.30 [J_{AX}=10.6 Hz] / 5.40 [J_{MX}= 2.2 Hz]		
H-1′×2		3.10 (q, J=7.7 Hz)	3.22 (t, J=7.3 Hz)
H-2′×3		1.30 (t, J=7.7 Hz)	H2′×2 3.87 (t, J=7.3 Hz)
H-3′×4			2.61 (q, J=7.1 Hz)
H-4′×6			1.00 (t, J=7.1 Hz)
C4-OCH_3	4.11 (s)	4.05 (s)	4.06 (s)
C8-OH	10.03 (s)[a]	9.95 (s)[a]	10.02 (s)[a]

I, II, and III in DMSO-d_6 solution. *a*) Disappeared with D_2O.

TABLE II. ^{13}C-NMR Spectral Data for Compounds I and II

Carbon	I	II
C-1	134.52	140.60
C-3	120.31	119.52
C-4	150.70	149.70
C-4a	117.62	116.86
C-4b	121.68	121.95
C-5	114.01	113.95
C-6	120.99	120.02
C-7	111.38	110.90
C-8	143.49	143.52
C-8a	129.69	129.48
C-9a	133.35	134.35
C-1′	132.00	25.82
C-2′	115.20	12.96
4-OCH_3	56.07	55.80

I and II in DMSO-d_6 solution.

TABLE III. ^{13}C-NMR Spectral Data for III

Carbon			^1J	^2J	^3J
C-1	137.89	m		3 (C1-H1′)	11 (C1-H2′)
C-3	119.09	d	176		
C-4	149.03	qi		5 (C4-H3)	5 (C4-OCH_3)
C-4a	116.38	d			5 (C4a-H3)
C-4b	121.40	d			10 (C4b-H6)
C-5	113.43	dd	160		8 (C5-H7)
C-6	119.40	d	160		
C-7	110.35	dd	157		8 (C7-H5)
C-8	142.92	dt		3 (C8-H7, OH)	11 (C8-H6)
C-8a	128.96	t			8 (C8a-H5, 7)
C-9a	134.47	s			
C-1′	30.51	td	127	3 (C1′-H2′)	
C-2′	51.44	tq	123		6 (C1′-H3′)
C-3′×2	45.96	tq	133		6 (C3′-H1′)
C-4′×2	11.65	qd	123	3 (C4′-H3′)	
4-OCH_3	55.56	qd	144		

Coupling constants in Hz. III in DMSO-d_6 solution.

K should be represented by formula III.

The assignments of ^{13}C resonances to the carbon atoms of picrasidine K were based on proton-noise and single frequency off-resonance decoupled spectra, one-bond selective proton decoupling (SPD), and long-range selective proton decoupling (LSPD) experiments. Carbons bearing protons were confirmed by SPD experiments and long-range couplings were confirmed by LSPD experiments. In the SPD experiments on picrasidine K, based on irradiation of the six aliphatic proton resonances at δ 1.00 (6H, t, H-4′), 2.61 (4H, q, H-3′), 2.87 (2H, t, H-2′), and 3.22 (2H, t, H-1′), the aliphatic carbon signals were concluded to be at δ 11.65 (×2), 45.96 (×2), 30.51, and 51.44, respectively. The values of one-bond ^{13}C–^{1}H coupling constants ($^1J_{CH}$) of C-5, -6, and -7 were observed within the range of 157—160 Hz. The value of 176.5 Hz for $^1J_{C3\text{-}H}$ is larger than the others because of the effect of the neighboring N atom. In the LSPD experiments on picrasidine K, irradiation of H-3 at δ 7.91

caused large changes at δ 149.03 (quintet, $^2J_{CH}=5$ and $^3J_{CH}=5$ Hz) and 116.38 (d, $^3J_{CH}=5$ Hz). The former signal changed into a quartet ($^3J_{CH}=5$ Hz) and the latter changed into a singlet. Therefore the signals were concluded to be due to C-4 and C-4a. Irradiation of 6-H at δ 7.02 caused the signal at δ 121.40 (d, $^3J_{CH}=10$ Hz) to change into a singlet. Irradiation of H-7 at δ 6.92 caused the signal at δ 128.96 (t, $^3J_{CH}=8$ Hz) to change into a doublet ($^3J_{CH}=8$ Hz). Irradiation of H-2′ at δ 2.87 caused the signals at δ 137.89 (multiplet) to change into a doublet triplet ($^2J_{CH}=3$ and $^3J_{CH}=11$ Hz). Therefore, the signal were concluded to be due to C-4b, C-8a, and C-1. Consequently, the unchanged carbon signal at δ 134.47 was assigned to C-9a. On the bases of the data for picrasidine K, seven quaternary carbon atoms were unambiguously assigned.

This is the first report of the isolation of 8-hydroxy-β-carboline alkaloids from Simaroubaceous plants.

Experimental

All melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. The UV and IR spectra were recorded with Hitachi 340 and Hitachi 260-30 spectrophotometers, respectively. The ^{1}H-NMR and carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra were recorded with JEOL GX-400 (^{1}H: 400 MHz and ^{13}C: 100 MHz) and Hitachi R-900 (^{1}H: 90 MHz) spectrometers. Chemical shifts are given on the δ scale (ppm) with tetramethylsilane as an internal standard, and coupling constants are given in Hz. The following abbreviations are used: s=singlet, d=doublet, dd=double doublet, t=triplet, q=quartet, qi=quintet, dt=doublet triplet, td=triplet doublet, tq=triplet quartet, qd=quartet doublet, m=multiplet, and sh=shoulder. Mass spectra were measured with a JEOL JMS-01SG-2 mass spectrometer. Column chromatography was carried out on Aluminum Oxide C-300 (Wako) and Silica gel 60 (Merck). Preparative chromatographies were performed on silica gel (Merck, 25×310 mm) and reversed phase Rp-8 (Merck, 25×310 mm) columns. Thin layer chromatography (TLC) was performed on precoated Silica gel F_{254} plates (Merck) and the spots were detected by using Dragendorff's reagent or by UV illumination.

Extraction and Isolation——Dried bark (7.5 kg) of *Picrasma quassioides* collected at Chiba city, Chiba prefecture in August, 1983 was extracted with MeOH (70 l) at 35 °C for 48 h. The extract was evaporated to dryness and the residue was partitioned between water and $CHCl_3$. The $CHCl_3$ solution was dried over Na_2SO_4 and concentrated to give a $CHCl_3$-soluble fraction (195 g) which was applied to a column of aluminum oxide (2.0 kg) and eluted successively with $CHCl_3$ and MeOH. The fractions (85 g) eluted with $CHCl_3$ were shaken with 3% H_2SO_4. The aqueous layer was basified with 5% Na_2CO_3 and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water, dried over Na_2SO_4, then concentrated to give a basic fraction (9.5 g), which was applied to a column packed with silica gel (180 g). The column was eluted successively with $CHCl_3$, 1, 2, 5, 10, 20, 50% MeOH in $CHCl_3$, and MeOH. The fractions (845 mg) eluted with 2% MeOH in $CHCl_3$ was further purified by preparative chromatography on silica gel (25×310 mm) with 5% MeOH in $CHCl_3$ as an eluent (2.0 ml/min) to give crystals. Recrystallization from $CHCl_3$–MeOH (1 : 1) give picrasidine I (65 mg). The fractions (760 mg) eluted with 5% MeOH in $CHCl_3$ were further purified by preparative chromatography on silica gel (25×310 mm) with 5% MeOH in $CHCl_3$ as an eluent (2.0 ml/min) to give crystals. Recrystallization from $CHCl_3$–MeOH (1 : 1) gave picrasidine J (60 mg). The fractions (3.1 g) eluted with 20% and 50% MeOH in $CHCl_3$ was further purified by preparative chromatography on an Rp-8 column (25×310 mm) with 10% triethylamine in MeOH as an eluent (1.0 ml/min) to give crystals. Recrystallization from MeOH gave picrasidine K (69 mg).

Picrasidine I (I)——Colorless plates, mp 240—241 °C (dec.). UV λ_{max}^{EtOH} nm (log ε): 230 (4.83), 252 (4.85), 268 (sh, 4.60), 360 (4.20). UV $\lambda_{max}^{EtOH+HCl}$ nm (log ε): 236 (4.78), 270 (4.70), 280 (sh, 4.65), 300 (sh, 4.42), 336 (4.16), 400 (3.94). UV $\lambda_{max}^{EtOH+NaOH}$ nm (log ε): 242 (4.78), 266 (4.61), 288 (sh, 4.42), 378 (3.90). IR ν_{max}^{KBr} cm^{-1}: 3420, 3320, 1640, 1585, 1490, 1410, 1275, 1145, 1015. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz): Tables I and II, respectively. MS *m/z* (%): 240 (M^+, 100), 239 (25), 225 (22), 224 (10), 198 (12), 197 (43), 170 (17), 169 (26), 120 (12). High-resolution MS: Calcd for $C_{14}H_{12}N_2O_2$, *m/z* 240.0899. Found: *m/z* 240.0885.

Acetylation of I——Compound I (20 mg) was acetylated with Ac_2O (0.2 ml) in pyridine (0.1 ml) at room temperature for 10 h. The product (20 mg) was crystallized from acetone to give 8-*O*-acetylpicrasidine I (IV) as colorless needles, mp 180—183 °C. MS *m/z* (%): 282 (M^+, 36), 240 (100), 197 (25). IR ν_{max}^{KBr} cm^{-1}: 3580, 1740, 1630, 1580, 1490, 1290, 1215, 1150. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 2.13 (3H, s, –COC$\underline{H}_3$), 4.06 (3H, s, C4-OC$\underline{H}_3$), 5.35, 6.17, 7.10 (AMX-system, $J_{AM}=18.0$ Hz, $J_{AX}=10.8$ Hz, $J_{MX}=2.0$ Hz, –CH=C$\underline{H}_2$), 7.18—7.23 (2H, m, H6, H7), 8.01 (1H, s, H3), 8.05 (1H, d, $J=8.0$ Hz, H5), 10.03 (1H, s, NH).

Methylation of I——Compound I (3 mg) was dissolved in tetrahydrofuran and methylated with diazomethane at room temperature for 48 h to give 8-*O*-methylpicrasidine I (VII, 3 mg), mp 158 °C. MS *m/z*: 254 (M^+). IR ν_{max}^{KBr} cm^{-1}:

3340, 1630, 1575, 1290, 1270, 1050. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 3.92 (3H, s, C8-OCH_3), 4.08 (3H, s, C4-OCH_3), 5.40, 6.22, 7.15 (AMX-system, $J_{AM}=17.5$ Hz, $J_{AX}=11.0$ Hz, $J_{MX}=2.2$ Hz, $-CH=CH_2$), 6.87 (1H, d, $J=8.0$ Hz, H7), 7.15 (1H, t, $J=8.0$ Hz, H6), 7.86 (1H, d, $J=8.0$ Hz, H5), 8.03 (1H, s, H3), 9.85 (1H, s, NH). The product was identified by direct comparison with an authentic sample[3] (TLC, IR spectra, and mixed melting point determination).

Picrasidine J (II)——Pale yellow prisms, mp 212—213 °C. UV λ_{max}^{EtOH} nm (log ε): 240 (4.50), 270 (3.46), 284 (3.46), 340 (3.46). UV $\lambda_{max}^{EtOH+HCl}$ nm (log ε): 256 (4.23), 318 (3.61), 370 (3.38). UV $\lambda_{max}^{EtOH+NaOH}$ nm (log ε): 254 (4.21), 280 (sh, 3.72), 352 (3.39). IR ν_{max}^{KBr} cm^{-1}: 3450, 3140, 1635, 1570, 1500, 1412, 1287, 1170, 1025. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz): Tables I and II, respectively. MS *m/z* (%): 242 (M^+, 100), 241 (62), 227 (68), 214 (13), 191 (32), 185 (16). High-resolution MS: Calcd for $C_{14}H_{14}N_2O_2$, *m/z* 242.1055. Found: *m/z* 242.0988.

Acetylation of II——Compound II (20 mg) was acetylated with Ac_2O (0.2 ml) in pyridine (0.1 ml) at room temperature for 10 h. The product (20 mg) was crystallized from acetone to give 8-*O*-acetylpicrasidine J (V) as colorless needles, mp 193—195 °C. MS *m/z* (%): 284 (M^+, 44), 242 (100), 227 (37), 199 (17). IR ν_{max}^{KBr} cm^{-1}: 3460, 1768, 1634, 1580, 1292, 1190, 1170, 1065. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.44 (3H, t, $J=7.5$ Hz, $-CH_2\underline{CH}_3$), 2.41 (3H, s, $COCH_3$), 3.16 (2H, q, $J=7.5$ Hz, $-\underline{CH}_2CH_3$), 4.01 (3H, s, C4-OCH_3), 7.32—7.34 (2H, m, H6 and H7), 7.92 (1H, s, H3), 8.23 (1H, d, $J=8.0$ Hz, H5).

Methylation of II——Compound II (3 mg) was dissolved in tetrahydrofuran and methylated with diazomethane for 48 h to give 8-*O*-methylpicrasidine J (VIII), mp 156 °C. MS *m/z*: 256 (M^+). IR ν_{max}^{KBr} cm^{-1}: 3140, 1575, 1290, 1270, 1160, 1070. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.37 (3H, t, $J=8.0$ Hz, $-CH_2\underline{CH}_3$), 3.10 (2H, q, $J=8.0$, $-\underline{CH}_2CH_3$), 3.85 (3H, s, C8-OCH_3), 4.02 (3H, s, C4-OCH_3), 6.83 (1H, d, $J=8.0$ Hz, 7H), 7.14 (1H, t, $J=8.0$ Hz, 6H), 7.90 (1H, d, $J=8.0$ Hz, 5H), 7.95 (1H, s, 3H), 9.64 (1H, s, NH). The product was identified by direct comparison with an authentic sample[2] (TLC, IR spectra, and mixed melting point determination).

Picrasidine K (III)——Colorless plates, mp 169—171 °C. UV λ_{max}^{EtOH} nm (log ε): 242 (4.77), 270 (sh, 4.03), 288 (sh, 3.88), 344 (3.75). UV $\lambda_{max}^{EtOH+HCl}$ nm (log ε): 260 (4.52), 328 (4.00), 384 (3.64). UV $\lambda_{max}^{EtOH+NaOH}$ nm (log ε): 256 (4.66), 282 (4.08), 356 (3.75). IR ν_{max}^{KBr} cm^{-1}: 3470, 3120, 2700, 1645, 1620, 1590, 1570, 1280, 1170, 1042, 800. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz): Tables I and III, respectively. MS *m/z* (%): 313 (M^+, 9), 240 (46), 225 (6), 197 (10), 169 (6), 86 (100), 58 (20). High-resolution MS: Calcd for $C_{18}H_{23}N_3O_2$, *m/z* 313.1790. Found: *m/z* 313.1758.

Acetylation of III——Compound III (10 mg) was acetylated with Ac_2O (0.2 ml) in pyridine (0.1 ml) at room temperature for 7.5 h to give 8-*O*-acetylpicrasidine K (VI, 10 mg). Pale yellow needles, mp 189—190 °C (VI-hydrochloride). MS *m/z* (%): 355 (M^+, 10), 313 (10), 240 (43), 197 (12), 86 (100). IR ν_{max}^{KBr} cm^{-1}: 3430, 1765, 1627, 1560, 1265, 1160, 1055. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.17 (6H, t, $J=7.0$ Hz, H4′), 2.45 (3H, s, $-COCH_3$), 2.82 (4H, q, $J=7.0$ Hz, H3′), 2.95 (2H, t, $J=6.0$ Hz, H1′), 3.38 (2H, t, $J=6.0$ Hz, H2′), 4.12 (3H, s, C4-OCH_3), 7.22 (1H, t, $J=8.0$ Hz, H6), 7.29 (1H, dd, $J=8.0$, 1.0 Hz, H7), 7.98 (1H, s, H3), 8.18 (1H, dd, $J=8.0$, 1.0 Hz), 11.41 (1H, s, NH).

Methylation of III——Compound III (5 mg) was dissolved in MeOH and methylated with diazomethane at room temperature for 48 h to give 8-*O*-methylpicrasidine K (IX, 5 mg). Pale yellow needles, mp 223—225 °C (IX-hydrochloride). MS *m/z* (%): 327 (M^+, 29), 255 (16), 241 (11), 199 (11), 86 (100). IR ν_{max}^{KBr} cm^{-1}: 3110, 1640, 1615, 1585, 1570, 1280, 1170. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.15 (6H, t, $J=7.1$ Hz, H4′), 2.75 (4H, q, $J=7.1$ Hz, H3′), 2.88 (1H, t, $J=2.0$ Hz, H1′), 2.88 (1H, d, $J=10.4$ Hz, H1′), 3.31 (1H, t, $J=2.0$ Hz, H2′), 3.31 (1H, d, $J=10.4$ Hz, H2′), 4.01 (3H, s, C8-OCH_3), 4.11 (3H, s, C4-OCH_3), 6.94 (1H, dd, $J=8.0$, 1.0 Hz, H7), 7.16 (1H, t, $J=8.0$ Hz, H6), 7.85 (1H, s, H3), 7.90 (1H, dd, $J=8.0$, 1.0 Hz, H5), 12.88 (1H, s, NH).

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References and Notes

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