*Chem. Pharm. Bull.* **46**(10) 1518—1521 (1998) Vol. 46, No. 10

# Four New Acridone–Coumarin Dimers from a *Citrus* Plant[1)]

Yuko TAKEMURA,[a] Junko TAKAYA,[a] Yuko OKAMURA,[a] Yasue ARIMA,[a] Tomomi ATARASHI,[a] Noriko NAGAREYA,[a] Motoharu JU-ICHI,*[,a] Mitsuo OMURA,[b] Chihiro ITO,[c] and Hiroshi FURUKAWA[c]

*Faculty of Pharmaceutical Sciences, Mukogawa Women's University,[a] Nishinomiya, Hyogo 663–8179, Japan, Okitsu Branch, Fruit Tree Research Station,[b] Ministry of Agriculture Forestry and Fisheries, Okitsu, Shimizu, Shizuoka 424–0292, Japan, and Faculty of Pharmacy, Meijo University,[c] Tempaku, Nagoya 468–8503, Japan.*

Received May 20, 1998; accepted July 3, 1998

**Four new acridone–coumarin dimers, neoacrimarines-H (1), -I (2), -J (3) and -K (4), were isolated from the roots of Marsh grapefruit (*Citrus paradisi* MACF.). The structures of these new compounds were elucidated by spectral analysis especially using heteronuclear multiple-bond correlation (HMBC) and nuclear Overhauser effect experiments.**

**Key words** *Citrus paradisi*; Rutaceae; acridone–coumarin dimer; neoacrimarine

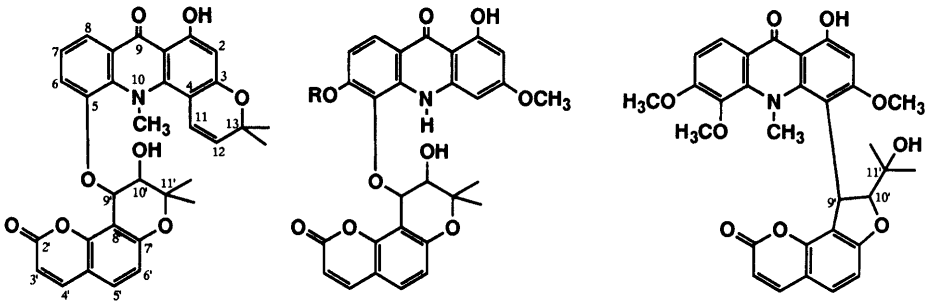
The roots of *Citrus* plants (Rutaceae) contain many kinds of coumarins and acridone alkaloids.[2)] Especially, acridone–coumarin dimers named acrimarines[3)] (composed of various acridone alkaloids and suberenol as a sole coumarin unit) and neoacrimarines[4)] (composed of various acridone alkaloids and coumarins except for suberenol) are characteristic constituents. In our continuing phytochemical studies of *Citrus* plants, we have already reported the isolation and structure elucidation of many new monomeric,[5)] dimeric acridone alkaloids[6)] and bicoumarins[7)] from the root of Marsh grapefruit (*C. paradisi* MACF.). On continuing our investigation of the constituents of this plant, we isolated an additional four new acridone–coumarin dimers, named neoacrimarines-H (**1**), -I (**2**), -J (**3**) and -K (**4**). We report here the structure elucidation of these new compounds.

The acetone extract of the root of Marsh grapefruit (*C. paradisi* MACF.) was fractionated by a combination of silica gel column and preparative thin layer chromatographies to give new acridone–coumarin dimers along with known coumarins and acridone alkaloids.

Neoacrimarine-H (**1**) was obtained as a yellow oil, $[\alpha]_D$ +80.6° ($CHCl_3$), and the molecular formula was determined as $C_{33}H_{28}NO_8$ by HR FAB-MS which showed an $[M+H]^+$ peak at *m/z* 568.1934 ($C_{33}H_{29}NO_8$). The UV [204, 265, 286, 294 (sh), 318, 343 (sh), 410 nm] and IR (1734, 1633, 1606, 1558 $cm^{-1}$) spectra suggested the presence of acridone and coumarin skeletons.[8)] The $^1$H-NMR spectrum showed the signal of a hydrogen-bonded hydroxyl group at $\delta$ 14.08 (1H, s), which is characteristic to the 1-hydroxy-9-acridone skeleton. The ABC type aromatic proton signals at $\delta$ 8.12 (1H, dd, $J$=7.9, 1.2 Hz), 7.78 (1H, dd, $J$=7.9, 1.2 Hz) and 7.38 (1H, t, $J$=7.9 Hz) were assigned to H-8, H-6 and H-7 of the acridone moiety, because the lowest signal was deshielded by a 9-carbonyl group. Two pairs of doublets at $\delta$ 7.47, 5.96 (each 1H, d, $J$=9.2 Hz) and $\delta$ 7.37, 6.87 (each 1H, d, $J$=8.5 Hz) were characteristic signals of H-4′, H-3′, H-5′ and H-6′ of the coumarin skeleton.[9)] Two olefinic proton signals at $\delta$ 5.89 and 5.34 (each 1H, d, $J$=9.2 Hz) and two methyl signals at $\delta$ 1.44 and 1.43 (each 3H, s) indicated the presence of a 2,2-dimethylpyran ring and two methine signals at $\delta$ 5.77 (1H, d, $J$=4.9 Hz) and 4.07 (1H, dd, $J$=4.9, 7.9 Hz), hydroxyl signal at $\delta$ 2.78 (1H, d, $J$=7.9 Hz) and two methyl signals at $\delta$ 1.61 and 1.53 (each 3H, s) suggested the presence of a 3,4-dioxygenated-2,2-dimethyl-dihydropyran ring. In differential nuclear Overhauser effect (NOE) experiments, irradiation of the signal at $\delta$ 3.46 (3H, s) induced an 8% increment of the olefinic proton signal at $\delta$ 5.89, suggesting the presence of an *N*-methyl group and an angular orientation for the 2,2-dimethylpyran ring of the acridone moiety. Thus, the lone aromatic proton signal at $\delta$ 6.21 was assigned to H-2. From the above results, the acridone and coumarin skeleton were presumed to be linked between C-5 and C-9′ by oxygen. We applied the heteronuclear multiple-bond correlation (HMBC) experiment to confirm the structure of neoacrimarine-H (**1**). Though no correlations were observed between methine signals [$\delta$ 5.77, 4.07] and any carbon signals, the observed $^2J$ and $^3J$ correlations (Fig. 1) supported the structure of both the acridone and the coumarin moieties. Irradiation of the methine signal at $\delta$ 5.77 caused a 10% enhancement of the signal at $\delta$ 4.07, indicating the *cis* relationship of two methine protons. From the above results, the structure of neoacrimarine-H was concluded to be **1**. The structural components of neoacrimarine-H (**1**) are the previously known acridone, 5-hydroxynoracronycine (**5**)[10)] and coumarin, *cis*-khellactone (**6**).[11)]

Neoacrimarine-I (**2**) was isolated as a yellow oil, $[\alpha]_D$ −157.3° ($CHCl_3$). The molecular formula $C_{29}H_{25}NO_9$ was obtained by HR FAB-MS which showed an $[M+H]^+$ peak at *m/z* 532.1584 ($C_{29}H_{26}NO_9$). The UV and IR absorption bands (see Experimental) indicated the presence of acridone and coumarin moieties.[8)] The presence of a 1,3,5,6-tetraoxygenated acridone nucleus in this molecule was suggested by the appearance of the signals of chelated hydroxyl group [$\delta$ 14.31 (1H, s)], *ortho*-coupled [$\delta$ 7.92, 6.96 (each 1H, d, $J$=9.2 Hz)] and *meta*-coupled [$\delta$ 6.43, 6.16 (each 1H, d, $J$=2.2 Hz)] aromatic protons in the $^1$H-NMR spectrum. The proton signals due to the coumarin moiety were similar to that of **1**, and showed the characteristic signals of H-4′, H-3′, H-5′ and H-6′ of the coumarin skeleton [$\delta$ 7.97, 6.17 (each 1H, d, $J$=9.2 Hz), 7.61, 6.85 (each 1H, d, $J$=8.8 Hz)] and the signals due to a 3,4-dioxygenated-2,2-dimethyldihydropyran ring [$\delta$ 5.45 (1H, d, $J$=3.7 Hz), 4.24 (1H , t , $J$=3.7 Hz), 1.61 (3H , s), 1.55 (3H , s)]. The presence of two methoxy groups was apparent from the signals at $\delta_H$ 3.88 and 3.42 in the $^1$H-

* To whom correspondence should be addressed.



neoacrimarine-H (1)

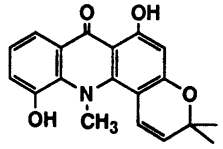


neoacrimarine-I (2) R=$CH_3$

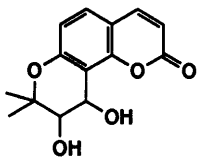
neoacrimarine-J (3) R=H



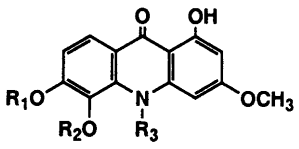
neoacrimarine-K (4)



5-hydroxynoracronycine (5)



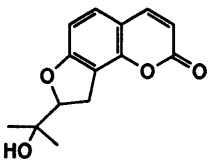
*cis*-khellactone (6) ; 9, 10:*cis*



grandisine-I (7) $R_1$=$CH_3$, $R_2$=$R_3$=H

des-6-O-methylgrandisine-I (8) $R_1$=$R_2$=$R_3$=H

citpressine-II (9) $R_1$=$R_2$=$R_3$=$CH_3$



columbianetin (10)

Chart 1

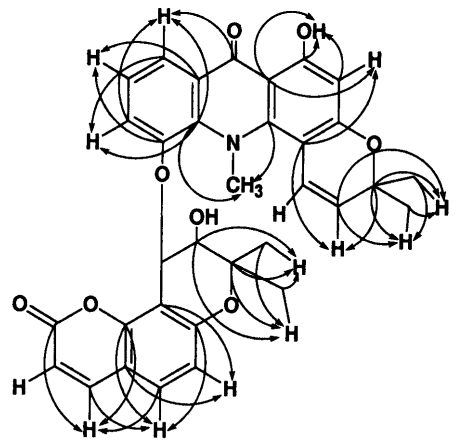


Fig. 1. C–H Long-Range Correlations in the HMBC Spectrum of Neoacrimarine-H (1)

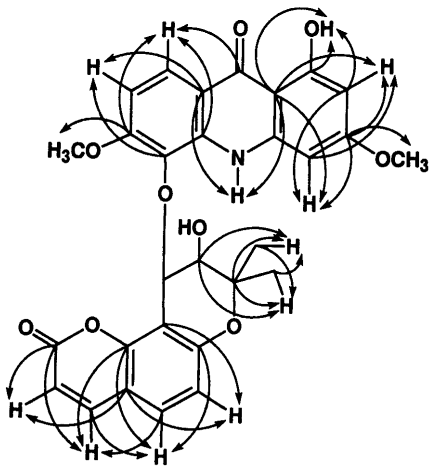


Fig. 2. C–H Long-Range Correlations in the HMBC Spectrum of Neoacrimarine-I (2)

NMR and $\delta_C$ 55.7 and 55.5 in the $^{13}$C-NMR spectra. In the NOE differential experiments (solvent: $CDCl_3$), irradiation of the signal at $\delta$ 4.04 caused a 13% enhancement of the signal at $\delta$ 6.97 (H-7). When the signal at $\delta$ 3.82 was irradiated, 9 and 7% enhancements of the signals at $\delta$ 6.23 (H-4) and 6.17 (H-2) were observed. Thus, the two methoxy groups were assigned to C-3 and C-6. Irradiation of the methine proton signal at $\delta$ 5.51 (H-9′) induced a 9% increment of the signal at $\delta$ 3.77 (H-10′), thus the *cis*-relationship of these protons was established. The $^2J$ and $^3J$ correlations obtained by HMBC experiment (Fig. 2) established the structures of both the acridone and the coumarin moieties, and the linkage between C-5 and C-9′ by oxygen was demonstrated. From the above results, we assigned the structure **2** to neoacrimarine-I. Neoacrimarine-I (**2**) corresponds to a dimer of grandisine-I (**7**)[12] and *cis*-khellactone (**6**).[11]

Neoacrimarine-J (**3**) was isolated as a yellow oil, $[\alpha]_D$ −131.9° ($CHCl_3$). The HR FAB-MS showed an $[M+H]^+$ peak at *m/z* 518.1463 which showed the molecular formula $C_{28}H_{23}NO_9$, a difference of $CH_2$ compared with neoacrimarine-I (**2**). The UV and IR spectra (see Experimental) indicated the presence of acridone and coumarin moieties.[8] The

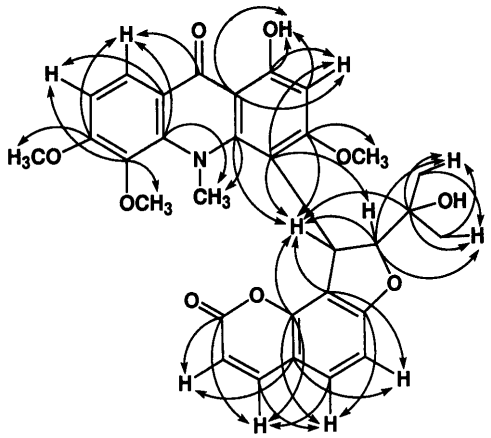


Fig. 3. C–H Long-Range Correlations in the HMBC Spectrum of Neoacrimarine-K (**4**)

$^1$H-NMR spectrum of **3** showed similar signal patterns to that of neoacrimarine-I (**2**), except for a lack of one methoxy group. In the differential NOE experiments, irradiation of the methoxy signal at $\delta$ 3.83 caused a 15% increment of the signal at $\delta$ 6.23 (2H, s, H-2, H-4), indicating the location of the methoxy group at C-3. On irradiation of the methine proton signal at $\delta$ 5.43, a 5% enhancement of the signal at $\delta$ 3.86 was induced. Inversely, irradiation of the signal at $\delta$ 3.86 caused a 5% enhancement of the signal at $\delta$ 5.43. These results indicated the *cis* relationship of the two methine protons. Based on these results, neoacrimarine-J was assigned the structure **3**. Neoacrimarine-J (**3**) corresponds to a dimer of unknown des-6-*O*-methylgrandisine-I (**8**)[13] and *cis*-khellactone (**6**).[11]

Neoacrimarine-K (**4**) was isolated as a yellow oil, racemate. The UV and IR spectra (see Experimental) suggested the presence of acridone and coumarin skeletons.[8] The HR EI-MS gave a molecular ion at *m/z* 559.1828, consistent with a molecular formula $C_{31}H_{29}NO_9$. The $^1$H-NMR spectrum showed characteristic signals due to chelated hydroxyl group [$\delta$ 14.36 (1H, s)], H-8 and H-7 [$\delta$ 8.07, 6.98 (each 1H, d, $J$=8.6 Hz)] and a lone aromatic proton [$\delta$ 6.30 (1H, s)] on the acridone skeleton, and H-4′, H-3′, H-5′ and H-6′ [$\delta$ 7.60, 6.10 (each 1H, d, $J$=9.2 Hz), 7.28, 6.80 (each 1H, d, $J$=8.5 Hz)] on the coumarin moiety. The presence of an *N*-methyl and three methoxy groups was apparent from the signals at $\delta_H$ 4.16 (3H, s), 4.01 (3H, s), 3.98 (3H, s), 3.57 (3H, s) in the $^1$H-NMR and $\delta_C$ 49.9, 56.2, 60.9 and 55.6 in the $^{13}$C-NMR spectra. In the differential NOE experiments, irradiation of the methoxy signal at $\delta$ 3.57 (3-MeO) caused a 24% increment of the signal at $\delta$ 6.30 (1H, s), providing the assignment of this proton as H-2. Irradiation of the *N*-methyl signal at $\delta$ 4.16 induced a 15% increment of the signal at $\delta$ 5.49 (H-9′). Irradiation of the methoxy signal at $\delta$ 4.01 (6-MeO) caused a 16% enhancement of the signal at $\delta$ 6.98 (H-7) and no NOE was observed on irradiation of the methoxy signal at $\delta$ 3.98 (5-MeO), suggesting the location of these two methoxy groups at C-6 and C-5. The signals at $\delta_H$ 5.49 (1H, d, $J$=7.3 Hz), 5.29 (1H, s), 4.46 (1H, d, $J$=7.3 Hz), 1.27 (3H, s), 1.05 (3H, s) in the $^1$H-NMR spectrum, coupled with signals at $\delta_C$ 41.4 (d), 97.8 (d), 72.1 (s), 26.3 (q) and 24.0 (q) in the $^{13}$C-NMR spectrum suggested the presence of a 3-substituted 2-hydroxyisopropyl-dihydrofuran ring system attached to C-7 and C-8 on the coumarin skeleton. From the above results, a linkage was assumed between C-4 of the acridone skeleton and C-9′ of the coumarin moiety. In order to confirm the structure, HMBC experiments were carried out. The methine proton signal at $\delta$ 5.49 showed correlations with the carbon signals at $\delta_C$ 151.1 (C-4a), 109.0 (C-4), 165.4 (C-3), 150.9 (C-8′a), 117.2 (C-8′), 97.8 (C-10′) and 72.1 (C-11′), supported the linking position of the two moieties. Other correlations observed in the HMBC experiments shown by arrows in Fig. 3 also supported the structure **4**. Because no increments were observed between the two methine signals at $\delta$ 4.46 and 5.49 in the NOE experiments, the relative configuration of H-9′ and H-10′ was assigned as *trans*. These spectral data led us to assign structure **4** to neoacrimarine-K, corresponding to a dimer of citpressine-II (**9**)[13] and columbianetin (**10**).[14] Among the neoacrimarines, neoacrimarine-K (**4**) is the first example that contains a dihydrofuranocoumarin moiety.

While the optical rotation of neoacrimarine-H (**1**) showed dextrorotatory, neoacrimarine-I (**2**) and -J (**3**) exhibited levorotatory. It may be due to the opposite stereostructure of *cis*-khellactone (**6**) moiety. The absolute stereochemistry of the four new compounds in this paper remains to be determined.

**Experimental**

$^1$H- and $^{13}$C-NMR spectra were recorded on GX-400 and GSX-500 (JEOL) spectrometers. Chemical shifts are shown on the $\delta$ (ppm) scale with tetramethylsilane (TMS) as an internal reference. Heteronuclear multiple quantum coherence (HMQC) and HMBC spectra were measured at $J$=8 Hz on an A-400 or A-600 (JEOL) spectrometer. EI- and HR-MS were taken with a Hitachi M-80 spectrometer having a direct inlet system. FAB- and HR FAB-MS were measured with a JMS-HX 110 spectrometer. UV spectra were recorded on a UV-160A (Shimadzu) or UVIDEC-610C double-beam spectrometer (Jasco) and IR spectra on a IR-450 (Shimadzu) or IR-230 (Jasco) spectrometer. Optical rotations were taken on a DIP-370 (Jasco).

**Isolation** The $CH_2Cl_2$ eluate (see the preceding paper[6a]) was further submitted to a combination of silica gel column chromatography and preparative TLC [solvent: benzene–AcOEt (1 : 1); $CHCl_3$–acetone (9 : 1); benzene–MeOH (9 : 1); benzene–AcOEt (6 : 4), AcOEt–*n*-hexane (1 : 1) to give neoacrimarine-H (**1**) (1.0 mg), -I (**2**) (2.1 mg) and -K (**3**) (3.2 mg). The acetone eluate (see the preceding paper[6a]) was worked up in a similar manner as above to give neoacrimarine-J (**4**) (1.3 mg).

Neoacrimarine-H (**1**): Yellow oil, $[\alpha]_D$ +80.6° ($c$=0.067, $CHCl_3$). UV $\lambda_{max}$ (MeOH) nm: 204, 265, 286, 294 (sh), 318, 343 (sh), 410. IR $\nu_{max}$ ($CHCl_3$) cm$^{-1}$: 1734, 1633, 1606, 1558. HR FAB-MS *m/z* 568.1934 $[M+H]^+$ (Calcd for $C_{33}H_{29}NO_8$: 568.1971). EI-MS *m/z*: 567 $[M]^+$, 323, 308 (base peak), 293, 244, 188, 160. $^1$H-NMR ($CDCl_3$, $\delta$) : 14.08 (1H, s, 1-OH), 8.12 (1H, dd, $J$=7.9, 1.2 Hz, H-8), 7.78 (1H, dd, $J$=7.9, 1.2 Hz, H-6), 7.47 (1H, d, $J$=9.2 Hz, H-4′), 7.38 (1H, t, $J$=7.9 Hz, H-7), 7.37 (1H, d, $J$=8.5 Hz, H-5′), 6.87 (1H, d, $J$=8.5 Hz, H-6′), 6.21 (1H, s, H-2), 5.96 (1H, d, $J$=9.2 Hz, H-3′), 5.89 (1H, d, $J$=9.2 Hz, H-11), 5.77 (1H, d, $J$=4.9 Hz, H-9′), 5.34 (1H, d, $J$=9.2 Hz, H-12), 4.07 (1H, dd, $J$=7.9, 4.9 Hz, H-10′), 3.46 (3H, s, N-Me), 2.78 (1H, d, $J$=7.9 Hz, 10′-OH), 1.61 (3H, s, 11′-Me), 1.53 (3H, s, 11′-Me), 1.44 (3H, s, 13-Me), 1.43 (3H, s, 13-Me). $^{13}$C-NMR ($CDCl_3$, $\delta$): 182.1 (s, C-9), 164.6 (s, C-1), 161.2 (s, C-3), 158.8 (s, C-2′), 156.4 (s, C-7′), 154.5 (s, C-8′a), 150.6 (s, C-5), 147.6 (s, C-4a), 142.9 (d, C-4′), 140.7 (s, C-10a), 129.5 (d, C-5′), 125.9 (s, C-8a), 124.0 (d, C-7), 123.7 (d, C-12), 122.1 (d, C-6), 120.7 (d, C-11), 120.4 (d, C-8), 114.7 (d, C-6′), 112.9 (d, C-3′), 112.4 (s, C-4′a), 108.2 (s, C-8′), 107.4 (s, C-9a), 102.5 (s, C-4), 98.5 (d, C-2), 78.9 (s, C-11′), 77.2 (d, C-9′), 76.5 (s, C-13), 70.7 (d, C-10′), 49.7 (q, N-Me), 27.2 (q, 13-Me), 27.0 (q, 13-Me), 25.8 (q, 11′-Me), 21.7 (q, 11′-Me).

Neoacrimarine-I (**2**): Yellow oil, $[\alpha]_D$ −157.3° ($c$=0.273, $CHCl_3$). UV $\lambda_{max}$ (MeOH) nm: 205, 255 (sh), 266, 292 (sh), 326, 381. IR $\nu_{max}$ ($CHCl_3$): 1734, 1643, 1604 cm$^{-1}$. HR FAB-MS *m/z* 532.1584 $[M+H]^+$ (Calcd for $C_{29}H_{26}NO_9$: 532.1608). FAB-MS *m/z*: 532 $[M+H]^+$, 369, 277, 185 (base peak), 93. $^1$H-NMR (DMSO-$d_6$, $\delta$) : 14.31 (1H, s, 1-OH), 12.15 (1H, s, NH), 7.97 (1H, d, $J$=9.2 Hz, H-4′), 7.92 (1H, d, $J$=9.2 Hz, H-8), 7.61 (1H, d,

$J$=8.8 Hz, H-5′), 6.96 (1H, d, $J$=9.2 Hz, H-7), 6.85 (1H, d, $J$=8.8 Hz, H-6′), 6.43 (1H, d, $J$=2.2 Hz, H-4), 6.17 (1H, d, $J$=9.2 Hz, H-3′), 6.16 (1H, d, $J$=2.2 Hz, H-2), 5.45 (1H, d, $J$=3.7 Hz, H-9′), 4.24 (1H, t, $J$=3.7 Hz, H-10′), 3.88 (3H, s, 3-MeO), 3.42 (3H, s, 6-MeO), 1.61 (3H, s, 11′-Me), 1.55 (3H, s, 11′-Me). ($CDCl_3$, $\delta$): 13.95 (1H, s, 1-OH), 9.7 (1H, br s, NH), 8.20 (1H, d, $J$=9.2 Hz, H-8), 7.62 (1H, d, $J$=9.2 Hz, H-4′), 7.40 (1H, d, $J$=8.5 Hz, H-5′), 6.97 (1H, d, $J$=9.2 Hz, H-7), 6.89 (1H, d, $J$=8.5 Hz, H-6′), 6.23 (1H, d, $J$=2.4 Hz, H-4), 6.18 (1H, d, $J$=9.2 Hz, H-3′), 6.17 (1H, d, $J$=2.4 Hz, H-2), 5.51 (1H, $J$=3.1 Hz, H-9′), 4.73 (1H, br s, 10′-OH), 4.04 (3H, s, 6-MeO), 3.82 (3H, s, 3-MeO), 3.77 (1H, m, H-10′), 1.62 (3H, s, 11′-Me), 1.52 (3H, s, 11′-Me). $^{13}$C-NMR (DMSO-$d_6$, $\delta$): 180.1 (s, C-9), 165.3 (s, C-3), 163.6 (s, C-1), 159.1 (s, C-2′), 156.1 (s, C-7′), 155.8 (s, C-6), 154.0 (s, C-8′a), 144.5 (d, C-4′), 142.9 (s, C-4a), 135.9 (s, C-10a), 133.5 (s, C-5), 129.9 (d, C-5′), 121.9 (d, C-8), 114.2 (s, C-8a), 113.8 (d, C-6′), 111.6 (d, C-3′), 111.5 (s, C-4′a), 109.3 (s, C-8′), 107.8 (d, C-7), 103.2 (s, C-9a), 94.5 (d, C-2), 89.5 (d, C-4), 79.2 (s, C-11′), 73.5 (d, C-10′), 70.8 (d, C-9′), 55.7 (q, 3-MeO), 55.5 (q, 6-MeO), 27.8 (q, 11′-Me), 21.8 (q, 11′-Me).

Neoacrimarine-J (**3**): Yellow oil, $[\alpha]_D$ −131.9° ($c$=0.046, $CHCl_3$). UV $\lambda_{max}$ (MeOH) nm: 203, 218 (sh), 263, 292 (sh), 327, 373 (sh). IR $\nu_{max}$ ($CHCl_3$) cm$^{-1}$: 1734, 1647, 1604, 1541, 1508. HR FAB-MS $m/z$ 518.1463 $[M+H]^+$ (Calcd for $C_{28}H_{24}NO_9$: 518.1451). FAB-MS $m/z$: 518 $[M+H]^+$, 274, 185, 93 (base peak). $^1$H-NMR ($CDCl_3$, $\delta$): 14.13 (1H, s, 1-OH), 10.13 (1H, s, NH), 8.12 (1H, d, $J$=8.5 Hz, H-8), 7.70 (1H, d, $J$=9.2 Hz, H-4′), 7.48 (1H, d, $J$=8.6 Hz, H-5′), 6.93 (1H, d, $J$=8.6 Hz, H-7), 6.92 (1H, d, $J$=8.5 Hz, H-6′), 6.33 (1H, d, $J$=9.2 Hz, H-3′), 6.23 (2H, s, H-2, H-4), 5.43 (1H, d, $J$=4.3 Hz, H-9′), 3.86 (1H, d, $J$=4.3 Hz, H-10′), 3.83 (3H, s, 3-MeO), 1.59 (3H, s, 11′-Me), 1.53 (3H, s, 11′-Me).

Neoacrimarine-K (**4**) : Yellow oil , $[\alpha]_D$ 0° ($c$=0.084 , $CHCl_3$). UV $\lambda_{max}$ (MeOH) nm : 204, 222 (sh), 261 (sh), 269, 334, 393. IR $\nu_{max}$ ($CHCl_3$), cm$^{-1}$: 1734, 1614, 1587. HR EI-MS: Calcd for $C_{31}H_{29}NO_9$ 559.1842. Found. 559.1828. EI-MS $m/z$: 559 $[M]^+$, 501, 500 (base peak), 486, 485. $^1$H-NMR ($CDCl_3$, $\delta$): 14.36 (1H, s, 1-OH), 8.07 (1H, d, $J$=8.6 Hz, H-8), 7.60 (1H, d, $J$=9.2 Hz, H-4′), 7.28 (1H, d, $J$=8.5 Hz, H-5′), 6.98 (1H, d, $J$=8.6 Hz, H-7), 6.80 (1H, d, $J$=8.5 Hz, H-6′), 6.30 (1H, s, H-2), 6.10 (1H, d, $J$=9.2 Hz, H-3′), 5.49 (1H, d, $J$=7.3 Hz, H-9′), 4.46 (1H, d, $J$=7.3 Hz, H-10′), 4.16 (3H, s, N-Me), 4.01 (3H, s, 6-MeO), 3.98 (3H, s, 5-MeO), 3.57 (3H, s, 3-MeO), 1.27 (3H, s, 11′-Me), 1.05 (3H, s, 11′-Me). $^{13}$C-NMR ($CDCl_3$, $\delta$): 182.8 (s, C-9), 165.4 (s, C-3), 164.6 (s, C-1), 164.4 (s, C-7′), 160.3 (s, C-2′), 157.7 (s, C-6), 151.1 (s, C-4a), 150.9 (s, C-8′a), 144.2 (s, C-10a), 144.1 (d, C-4′), 139.4 (s, C-5), 128.6 (d, C-5′), 122.3 (d, C-8), 119.2 (s, C-8a), 117.2 (s, C-8′), 113.0 (s, C-4′a), 112.0 (d, C-3′), 109.0 (s, C-4), 108.4 (d, C-7), 107.8 (s, C-9a), 106.4 (d, C-6′), 97.8 (d, C-10′), 95.4 (d, C-2), 72.1(s, C-11′), 60.9 (q, 5-MeO), 56.2 (q, 6-MeO), 55.6 (q, 3-MeO), 49.9 (q, N-Me), 41.4 (d, C-9′), 26.3 (q, 11′-Me), 24.0 (q, 11′-Me).

**Acknowledgements** We are grateful to Ms. K. Suwa and S. Takeyama, Mukogawa Women's University, for NMR and MS measurements. This work was supported in part by a Grant-in-Aid (to H. F., 1997) for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan.

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