# Three New Bicoumarins from *Citrus hassaku*[1)]

Yuko TAKEMURA,[a] Toshimi NAKATA,[a] Motoharu JU-ICHI,*[,a] Masayoshi OKANO,[b] Narihiko FUKAMIYA,[b] Chihiro ITO,[c] and Hiroshi FURUKAWA*[,c]

*Faculty of Pharmaceutical Sciences, Mukogawa Women's University,[a] Nishinomiya, Hyogo 663, Japan, Faculty of Integrated Arts and Sciences, Hiroshima University,[b] Higashihiroshima, Hiroshima 724, Japan, and Faculty of Pharmacy, Meijo University,[c] Tempaku, Nagoya 468, Japan.*

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**Three new bicoumarins named bisnorponcitrin (1), khelmarin-C (2), and bishassanidin (3) were isolated from the root of *Citrus hassaku* HORT. *ex* TANAKA (Rutaceae) and their structures were elucidated on the basis of spectroscopic analyses.**

**Keywords** bicoumarin; bisnorponcitrin; khelmarcin-C; bishassanidin; *Citrus hassaku*; Rutaceae

As a continuation of our phytochemical work on the constituents of *Citrus* plants, we have reported the isolation and structure elucidation of many kinds of new coumarins,[2)] acridone alkaloids[3)] and a flavanone.[4)] Bicoumarins and acridone–coumarin dimers (acrimarines and neoacrimarines) are characteristic constituents of *Citrus* plants. Further investigation of the constituents of *Citrus hassaku* HORT *ex* TANAKA has led us to isolate three additional new bicoumarins, named bisnorponcitrin (**1**), khelmarin-C (**2**), and bishassanidin (**3**). In this paper, we wish to report the isolation of these new bicoumarins and their structure elucidation by spectroscopic methods.

The acetone extract of the root bark of the plant was fractionated by using a combination of silica gel column chromatography and preparative thin layer chromatography (PTLC) to give bisnorponcitrin (**1**), khelmarin-C (**2**), and bishassanidin (**3**), along with known coumarins and acridone alkaloids.

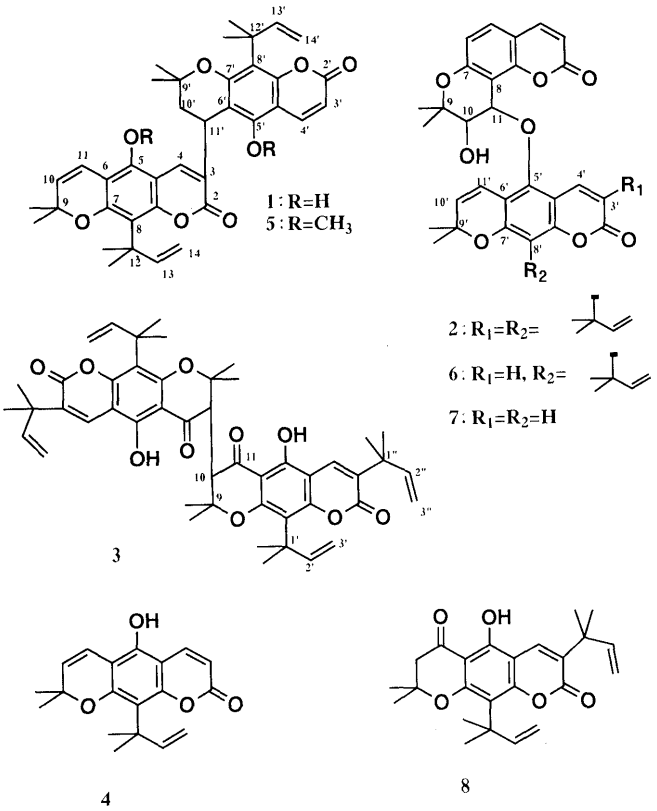
**Structure of Bisnorponcitrin (1)** Bisnorponcitrin (**1**) was isolated as light yellow prisms, $[\alpha]_D$ $\pm 0°$ ($CHCl_3$), mp 220—225 °C. The molecular formula $C_{38}H_{40}O_8$ was obtained from the high-resolution mass spectrum (HR-MS). The characteristic fluorescence observed on TLC, and the infrared (IR) absorptions at 1700, 1665 and 1595 $cm^{-1}$ and ultraviolet (UV) absorptions at 269, 288 and 330 nm indicated the presence of a coumarin nucleus.[5)] The proton magnetic resonance ($^1$H-NMR) spectrum showed characteristic AB-type signals of H-4 and H-3 of a coumarin nucleus [$\delta$ 7.98, 6.03 (each 1H, d, $J=9.4$ Hz)] and H-4 of 3-substituted coumarin ($\delta$ 7.85, 1H, s). The chemical shift of H-4 indicated the presence of an oxygen function at C-5.[6)] The $^1$H-NMR spectrum also exhibited signals attributable to a 2,2-dimethylpyran ring [$\delta$ 6.51, 5.68 (each 1H, d, $J=9.8$ Hz), 1.52 (6H, s)], and two 1,1-dimethylallyl groups [$\delta$ 6.28 (1H, dd, $J=17.5$, 10.7 Hz), 6.24 (1H, dd, $J=17.5$, 10.7 Hz), 4.95 (1H, dd, $J=17.5$, 0.9 Hz), 4.89 (1H, dd, $J=10.7$, 0.9 Hz), 4.87 (1H, dd, $J=17.5$, 0.9 Hz), 4.80 (1H, dd, $J=10.7$, 0.9 Hz), 1.66, 1.62, 1.44, 1.43 (each 3H, s)]. The remaining signals at $\delta$ 1.99, 2.33 (each 1H, dd, $J=13.7$, 8.5 Hz) and $\delta$ 4.43 (1H, t, $J=8.5$ Hz) indicated the presence of $-CH_2-CH-$ partial structure.

In the electron impact (EI)-MS, an intense peak was observed at $m/z$ 312 ($C_{19}H_{20}O_4$), corresponding to half of the molecular ion. Comparisons of these data with those for norponcitrin (nordentatin, **4**)[7)] suggested the structure of this compound to be a dimer of a pyranocoumarin such as norponcitrin (nordentatin, **4**). Because of its low solubility, **1** was treated with diazomethane to give the *O,O*-dimethylether (**5**) and further information was obtained by detailed spectral analyses of **5**.

The linking position and the linear or angular orientation of the pyran ring of the two coumarin moieties were clarified by nuclear Overhauser effect (NOE) experiments on the *O,O*-dimethylether (**5**). Irradiation of the methoxy signal at $\delta$ 3.62 (C-5) induced 7% and 8% increments of the signals at $\delta$ 6.50 (1H, d, $J=9.8$ Hz, H-11) and 7.27 (1H, s, H-4), respectively. When another methoxy signal at $\delta$ 3.69 (C-5′) was irradiated, an 8% increment was observed on each of the signals at $\delta$ 7.76 (1H, d, $J=9.5$ Hz, H-4′) and 4.47 (1H, dd, $J=7.3$, 10.3 Hz, H-11′). These results showed that both coumarin nuclei have a linearly oriented pyran ring and prove the compound to be a dimer of norponcitrin (nordentatin,[7)] **4**) and its dihydro compound linked between C-3 and 11′. Thus, the structure of bisnorponcitrin is **1**.

**Structure of Khelmarin-C (2)** Khelmarin-C (**2**) was isolated as a light yellow oil, $[\alpha]_D$ $-32.5°$ ($CHCl_3$). The molecular formula $C_{38}H_{40}O_8$ was given by HR-MS and the EI-MS showed prominent fragment peaks at $m/z$ 244 [$C_{14}H_{12}O_4$] amd 380 [$C_{24}H_{28}O_4$]. suggesting the binary structure of this compound. The IR absorptions at 1720, 1605 and 1590 $cm^{-1}$ and UV absorptions at 219 (sh), 277 and 328 nm showed characteristic absorptions of coumarin.[5)] The $^1$H-NMR spectrum showed characteristic signals of H-4, H-3 [$\delta$ 7.37, 5.93 (each 1H, d, $J=9.4$ Hz)], H-5, and H-6 [$\delta$ 7.29, 6.89 (each 1H, d, $J=8.7$ Hz)] of the coumarin skeleton and the signals attributable to a 2,2-dimethyldihydroxydihydropyran ring [$\delta$ 5.59 (1H, d, $J=4.4$ Hz), 4.10 (1H, dd, $J=4.4$, 11.4 Hz), 3.00 (1H, d, $J=11.4$ Hz, disappeared with $D_2O$), and 1.66, 1.69 (each 3H, s)]. From these data, the presence of a khellactone moiety was assumed. The remaining signals of a lone singlet ($\delta$ 7.18), two 1,1-dimethylallyl groups [$\delta$ 6.33 (1H, dd, $J=10.8$, 17.5 Hz)], 5.74 (1H, dd, $J=10.4$, 17.8 Hz), 4.96 (1H, d, $J=17.8$ Hz), 4.88 (1H, d, $J=10.8$ Hz), 4.91 (1H, d, $J=10.4$ Hz), 4.80 (1H, d, $J=17.5$ Hz), 1.65, 1.63, 1.25, 1.12 (each 3H, s)], and a 2,2-dimethylpyran ring [$\delta$

6.82, 5.75 (each 1H, d, $J=8.7$ Hz), 1.59, 1.49 (each 3H, s)] were similar to those of clausarin, suggesting the other coumarin moiety to be of clausarin type. Two bicoumarins named khelmarin-A (**6**) and -B (**7**) made up of khellactone and other coumarins have been reported.[8] Comparisons of the $^1$H-NMR data of **2** with those of **6** and **7** (Table I) showed similar signal patterns derived from the khellactone moiety. The differences were concluded to be due to the 1,1-dimethylallyl group attached to the linear coumarin moiety. These results led us to assign the structure **2** to khelmarin-C. The relative stereochemistry of C-10 and C-11 was assigned as *cis*, as in other khelmarins, on the basis of the relatively small coupling constants of H-10 and H-11 ($J=4.4$ Hz). The speculation was confirmed by NOE experiments. Irradiation of the signal at $\delta$ 4.10 (H-10) caused an 11% increment of the signal at $\delta$ 5.59 (H-11), suggesting the relative stereochemistry of the hydroxyl group (C-10) and the ether linkage to be *cis*. Khelmarin-C is the third example of a bicoumarin consisting of khellactone and another coumarin.




**Structure of Bishassanidin (3)** Bishassanidin (**3**) was isolated as a light yellow oil, $[\alpha]_D$ $\pm 0°$ ($CHCl_3$). The molecular formula was determined as $C_{48}H_{54}O_{10}$ by HR-MS. The IR absorptions at 1720, 1630 and 1610 cm$^{-1}$ and UV absorptions at 226 (sh), 293 and 331 nm indicated the presence of a coumarin moiety.[5] The $^1$H-NMR spectrum showed signals of a chelated hydroxyl group ($\delta$ 12.81, s), a lone aromatic proton ($\delta$ 7.89), and two 1,1-dimethylallyl groups [$\delta$ 6.26 (1H, dd, $J=10.3$, 17.6 Hz), 6.16 (1H, dd, $J=10.3$, 17.6 Hz), 5.13 (1H, dd, $J=1.5$, 10.3 Hz), 5.10 (1H, dd, $J=1.5$, 17.6 Hz), 4.96 (1H, dd, $J=1.5$, 17.6 Hz), 4.91 (1H, dd, $J=1.5$, 10.3 Hz), 1.66, 1.65 (each 3H, s) and 1.47 (6H, s)]. The remaining signals at $\delta$ 2.93 (1H, s), 1.63, and 1.45 (each 3H, s) were assumed to be due to protons of the 2,2-dimethylpyrone ring. Because the number of proton signals was half that expected, this coumarin was considered to have symmetric binary structure. As shown in Table II, the $^1$H-NMR signals were very similar to signals described previously

TABLE I. $^1$H-NMR Data for Khelmarins-C (**2**), -A, (**6**) and -B (**7**) in $CDCl_3$

| | 2 | 6 | 7 |
|---|---|---|---|
| H-3 | 5.93 (d, 9.4) | 5.95 (d, 9.5) | 5.96 (d, 9.5) |
| H-4 | 7.37 (d, 9.4) | 7.41 (d, 9.5) | 7.43 (d, 9.5) |
| H-5 | 7.29 (d, 8.7) | 7.30 (d, 8.7) | 7.32 (d, 8.7) |
| H-6 | 6.89 (d, 8.7) | 6.79 (d, 8.7) | 6.80 (d, 8.7) |
| 9-Me | 1.66 (3H, s) | 1.64 (3H, s) | 1.65 (3H, s) |
| | 1.69 (3H, s) | 1.68 (3H, s) | 1.69 (3H, s) |
| H-10 | 4.10 (dd, 4.4, 11.4) | 4.10 (dd, 4.4, 11.0) | 4.11 (dd, 4.4, 11.0) |
| 10-OH | 3.00 (d, 11.4) | 3.04 (d, 11.0) | 2.98 (d, 11.0) |
| H-11 | 5.59 (d, 4.4) | 5.61 (d, 4.4) | 5.67 (d, 4.4) |
| H-3′ | — | 5.81 (d, 9.5) | 5.85 (d, 9.5) |
| H-4′ | 7.18 (br s) | 7.40 (br) | 7.38 (br d, 9.5) |
| H-8′ | — | — | 6.57 (s) |
| 9′-Me | 1.49 (3H, s) | 1.42 (3H, s) | 1.44 (3H, s) |
| | 1.59 (3H, s) | 1.54 (3H, s) | 1.55 (3H, s) |
| H-10′ | 5.75 (d, 8.7) | 5.64 (d, 10.3) | 5.67 (d, 10.3) |
| H-11′ | 6.82 (d, 8.7) | 6.75 (d, 10.3) | 6.73 (d, 10.3) |
| 8′-DMA[a] | 6.33 (dd, 10.8, 17.5) | 6.31 (dd, 10.5, 17.3) | — |
| | 4.80 (d, 17.5) | 4.94 (d, 17.3) | — |
| | 4.88 (d, 10.8) | 4.86 (d, 10.5) | — |
| | 1.65 (3H, s) | 1.65 (6H, s) | — |
| | 1.63 (3H, s) | | — |
| 3′-DMA[a] | 5.74 (dd, 10.4, 17.8) | — | — |
| | 4.96 (d, 17.8) | — | — |
| | 4.91 (d, 10.4) | — | — |
| | 1.25 (3H, s) | — | — |
| | 1.12 (3H, s) | — | — |

Values are in $\delta$ ppm. Figures in parentheses are coupling constants ($J$) in Hz.
*a*) DMA = 1,1-dimethylallyl.

TABLE II. $^{13}$C- and $^1$H-NMR Spectral Data of Bishassanidin (**3**) and Hassanidin (**8**)

| | 3 | | 8 | |
|---|---|---|---|---|
| | $\delta_C$ | $\delta_H$ | $\delta_C$ | $\delta_H$ |
| 2 | 159.20 | | 159.69 | |
| 3 | 130.11 | | 129.79 | |
| 4 | 132.43 | 7.89 (s) | 132.47 | 7.89 (s) |
| 4a | 104.11 | | 103.52 | |
| 5 | 158.61 | | 158.82 | |
| 5-OH | | 12.81 (s) | | 13.00 (s) |
| 6 | 105.18 | | 104.00 | |
| 7 | 158.94 | | 159.34 | |
| 8 | 114.27 | | 113.87 | |
| 8a | 158.75 | | 158.93 | |
| 9 | 83.57 | | 79.77 | |
| 9-Me | 22.51 | 1.45 (3H, s) | 26.53 | 1.48 (6H, s) |
| | 28.81 | 1.63 (3H, s) | | |
| 10 | 53.84 | 2.93 (s) | 47.85 | 2.74 (2H, s) |
| 11 | 196.44 | | 198.27 | |
| 1′ | 40.87 | | 40.94 | |
| 1′-Me | 29.20 | 1.65 (3H, s) | 30.88 | 1.63 (6H, s) |
| | 29.71 | 1.66 (3H, s) | | |
| 2′ | 149.59 | 6.26 (dd, 10.3, 17.6) | 149.63 | 6.23 (dd, 10.7, 17.6) |
| 3′ | 112.30 | 4.96 (dd, 1.5, 17.6) | 112.24 | 4.88 (dd, 10.7, 1.0) |
| | | 4.91 (dd, 1.5, 10.3) | | 4.93 (dd, 17.6, 1.0) |
| 1″ | 40.33 | | 40.30 | |
| 1″-Me | 26.08 | 1.47 (6H, s) | 26.08 | 1.47 (6H, s) |
| | 26.11 | | | |
| 2″ | 145.23 | 6.16 (dd, 10.3, 17.6) | 145.31 | 6.16 (dd, 17.6, 10.7) |
| 3″ | 108.41 | 5.10 (dd, 1.5, 17.6) | 108.31 | 5.09 (dd, 10.7, 1.0) |
| | | 5.13 (dd, 1.5, 10.3) | | 5.10 (dd, 17.6, 1.0) |

Values are in $\delta$ ppm. Figures in parentheses are coupling constants ($J$) in Hz.

for hassanidin (**8**)[9] except for the presence of singlet methine proton signal at $\delta$ 2.93 and the lack of the signal of methylene protons at $\delta$ 2.74. The $^{13}$C-NMR spectrum of **3** was also similar to that of **8** but showed the C-10 signal as a doublet at $\delta$ 53.84 instead of the triplet at $\delta$ 47.85. The above results led us to assign the structure **3** to bishassanidin.

Further investigations of the constituents of this plant are in progress.

## Experimental

Melting points were measured on a Yanagimoto melting point apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-360 polarimeter. UV spectra were measured on a Shimadzu UV-160A spectrometer and IR spectra were taken with a Shimadzu IR-435 spectrometer. NMR spectra were recorded on a JEOL 200FX or JEOL-GSX 500 spectrometer and chemical shifts are given on the $\delta$ (ppm) scale with tetramethylsilane (TMS) as an internal standard. For column chromatography, Wakogel 60 was used. PTLC was carried out on precoated Merck Kieselgel plates.

**Extraction and Isolation** The acetone extract (485 g)[10] of dried roots (3.2 kg) of *C. hassaku* HORT. *ex* TANAKA (Rutaceae) collected at Innoshima, Hiroshima, was subjected to silica gel chromatography eluted with hexane, benzene, $CH_2Cl_2$, acetone and MeOH, successively. The $CH_2Cl_2$ eluate (99.4 g) was subjected to preparative TLC with isopropyl ether to give **1** (16.0 mg) (0.000005%). The benzene eluate was subjected repeatedly to preparative TLC with isopropyl ether, $CHCl_3$–acetone (19 : 1), benzene–ethyl acetate (9 : 1), hexane–ethyl acetate (9 : 1) and hexane–acetone (8 : 2) as developing solvents to obtain **2** (4.6 mg) (0.00000144%) and **3** (3.3 mg) (0.00000103%).[11]

**Bisnorponcitrin (1)** Light yellow prisms, $[\alpha]_D$ $\pm 0°$ ($c$ = 0.410, $CHCl_3$), mp 220—225 °C. HR-MS Calcd for $C_{38}H_{40}O_8$: 624.2723. Found: 624.2720. EI-MS $m/z$ (%): 624 ($M^+$, 22), 609 (22), 556 (10), 313 (31), 312 (64), 311 (12), 298 (23), 297 (100, base peak), 269 (11), 245 (11), 241 (11), 229 (16), 213 (19). UV $\lambda_{max}^{EtOH}$ nm: 208, 269, 288, 330. IR ($CHCl_3$): 3300 (br), 1700, 1665, 1595, 1560 cm$^{-1}$. $^1$H-NMR ($CDCl_3$) $\delta$: 7.98 (1H, d, $J$ = 9.4 Hz), 7.85 (1H, s), 6.51 (1H, d, $J$ = 9.8 Hz), 6.43 (1H, br s), 6.28 (1H, dd, $J$ = 10.7, 17.5 Hz), 6.24 (1H, dd, $J$ = 17.5, 10.7 Hz), 6.23 (1H, br s), 6.03 (1H, d, $J$ = 9.4 Hz), 5.68 (1H, d, $J$ = 9.8 Hz), 4.95 (1H, dd, $J$ = 0.9, 17.5 Hz), 4.89 (1H, dd, $J$ = 0.9, 10.7 Hz), 4.87 (1H, dd, $J$ = 0.9, 17.5 Hz), 4.80 (1H, dd, $J$ = 0.9, 10.7 Hz), 4.43 (1H, t, $J$ = 8.5 Hz), 2.33 (1H, dd, $J$ = 13.7, 8.5 Hz), 1.99 (1H, dd, $J$ = 13.7, 8.5 Hz), 1.66, 1.62, 1.61 (each 3H, s), 1.52 (6H, s), 1.48, 1.44, 1.43 (each 3H, s).

***O,O*-Dimethylbisnorponcitrin (5)** Ethereal diazomethane (10 ml) prepared in the usual manner was added to a solution of bisnorponcitrin (**1**) (9.7 mg) in 10 ml of methanol, and the mixture was allowed to stand overnight at room temperature. The solvent was evaporated, and the residue was subjected to PTLC [*n*-hexane–acetone (8 : 2)] to give **5** as a light yellow oil. Yield 6.7 mg, $[\alpha]_D$ $\pm 0°$ ($c$ = 0.056, $CHCl_3$). HR-MS Calcd for $C_{40}H_{44}O_8$ 652.3036. Found: 652.3034. EI-MS $m/z$ (%): 652 ($M^+$, 91), 639 (13), 638 (48), 637 (100, base peak), 622 (14), 621 (30), 582 (10), 581 (24), 394 (18), 393 (59), 339 (10), 311 (25), 309 (11), 283 (16), 271 (11), 259 (21), 257 (15), 255 (11), 229 (10). UV $\lambda_{max}^{MeOH}$ nm: 212, 224 (sh), 264, 272, 333. IR ($CHCl_3$): 1720, 1620, 1590 cm$^{-1}$. $^1$H-NMR ($CDCl_3$) $\delta$: 7.76 (1H, d, $J$ = 9.5 Hz), 6.50 (1H, d, $J$ = 9.8 Hz), 6.33 (1H, dd, $J$ = 10.5, 17.6 Hz), 6.32 (1H, dd, $J$ = 10.5, 17.3 Hz), 6.16 (1H, d, $J$ = 9.5 Hz), 5.66 (1H, d, $J$ = 9.8 Hz), 4.97 (1H, dd, $J$ = 1.2, 17.6 Hz), 4.93 (1H, dd, $J$ = 1.2, 17.3 Hz), 4.89 (1H, dd, $J$ = 1.2, 10.5 Hz), 4.87 (1H, dd, $J$ = 1.2, 10.5 Hz), 4.47 (1H, dd, $J$ = 7.3, 10.3 Hz), 3.69, 3.62 (each 3H, s), 2.27 (1H, dd, $J$ = 13.7, 7.3 Hz), 1.86 (1H, dd, $J$ = 13.7, 10.3 Hz), 1.72, 1.71 (each 3H, s), 1.68 (6H, s), 1.44, 1.43, 1.42, 1.32 (each 3H, s). NOE: irradiation of the signal at $\delta$ 3.62 (5-MeO)—7% enhancement at $\delta$ 6.50 (H-11) and 8% increment at $\delta$ 7.27 (H-4); irradiation at $\delta$ 3.69 (5′-MeO)—8% enhancement at each of $\delta$ 7.76 (H-4′) and 4.47 (H-11′); irradiation at $\delta$ 4.47 (H-11′)—3% enhancement at $\delta$ 7.27 (H-4), 4% enhancement at $\delta$ 3.69 (5′-MeO) and 7% enhancement at $\delta$ 2.27 (H-10′). $^{13}$C-NMR ($CDCl_3$) $\delta$: 161.16 (s), 160.82 (s), 158.02 (s), 155.20 (s), 153.87 (s), 153.16 (s), 152.68 (s), 150.63 (s), 150.30 (d), 149.83 (d), 138.94 (d), 132.83 (d), 130.38 (d), 127.59 (s), 119.62 (s), 118.87 (s), 116.31 (d), 113.90 (s), 111.77 (s), 111.68 (d), 108.10 (t), 107.93 (s), 107.80 (t), 107.52 (s), 77.20 (s × 2), 63.22 (q), 62.20 (q), 41.52 (s), 41.18 (s), 40.35 (t), 30.68 (q), 29.93 (q), 29.36 (q), 29.30 (q × 2), 29.10 (q), 27.59 (q), 27.55 (q), 24.22 (d).

**Khelmarin-C (2)** Light yellow oil, $[\alpha]_D$ $-32.5°$ ($c$ = 0.209, $CHCl_3$). HR-MS Calcd for $C_{38}H_{40}O_8$: 624.2720. Found: 624.2715. EI-MS $m/z$ (%): 624 ($M^+$, 4), 381 (18), 380 (59), 366 (39), 365 (100, base peak), 297 (16), 244 (35), 203 (35), 201 (22), 188 (52), 187 (15). UV $\lambda_{max}^{MeOH}$ nm: 219 (sh), 265 (sh), 277, 328. IR ($CHCl_3$): 3400 (br), 1720, 1605, 1590 cm$^{-1}$. $^1$H-NMR ($CDCl_3$) $\delta$: see Table I. NOE: irradiation of the signal at $\delta$ 4.10 (H-10)—11% enhancement at $\delta$ 5.59 (H-11); irradiation at $\delta$ 5.59—10% enhancement at $\delta$ 4.10; irradiation at $\delta$ 6.82 (H-10′)—7% enhancement at $\delta$ 5.59 (H-11); irradiation at $\delta$ 7.18 (H-4′)—2% enhancement at $\delta$ 5.59 (H-11).

**Bishassanidin (3)** Light yellow oil, $[\alpha]_D$ $\pm 0°$ ($c$ = 0.300, $CHCl_3$). HR-MS Calcd for $C_{48}H_{54}O_{10}$: 790.3717. Found: 790.3704. EI-MS $m/z$ (%): 790 ($M^+$, 100, base peak), 775 (18), 722 (13), 449 (22), 396 (12), 395 (25), 381 (25), 379 (13), 341 (11), 339 (11), 325 (14). UV $\lambda_{max}^{EtOH}$ nm: 203, 226 (sh), 293, 331. IR ($CHCl_3$): 1720, 1630, 1610, 1570 cm$^{-1}$. $^1$H- and $^{13}$C-NMR ($CDCl_3$) $\delta$: see Table II.

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## References and Notes

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