# Schoepfiajasmins A–H: *C*-Glycosyl Dihydrochalcones, Dihydrochalcone Glycoside, *C*-Glucosyl Flavanones, Flavanone Glycoside and Flavone Glycoside from the Branches of *Schoepfia jasminodora*

Kouki Ukida,[a] Takashi Doi,[a] Sachiko Sugimoto,[a] Katsuyoshi Matsunami,[a] Hideaki Otsuka,*[,a,b] and Yoshio Takeda[b]

[a] *Graduate School of Biomedical and Health Sciences, Hiroshima University; 1–2–3 Kasumi, Minami-ku, Hiroshima 734–8553, Japan: and* [b] *Faculty of Pharmacy, Yasuda Women's University; 6–13–1 Yasuhigashi, Asaminami-ku, Hiroshima 731–0153, Japan.*

Received June 12, 2013; accepted August 23, 2013

**From the branches of *Schoepfia jasminodora* collected in Okinawa, three new dihydrochalcone *C*-glycosides, one dihydrochalcone di-*O*-glucopyranoside, two flavanone *C*-glycosides, one flavanone *O*-glycoside and one flavone *O*-glycoside were isolated. Their structures were elucidated by extensive study of one- and two-dimensional NMR spectroscopic data.**

**Key words** *Schoepfia jasminodora*; Olacaceae; chalcone; flavanone; flavone

*Schoepfia jasminodora* is the only species belonging to the Olacaceae growing wild in Japan. Leaves of *S. jasminodora*, collected in Okinawa, afforded the gallates of isoorientin and (2*S*)-1,2-propanediol glucoside. As expected from the presence of gallate in the molecules, the compounds isolated from the leaves showed strong 1,1-diphenyl-2-picrylhydrazil (DPPH) radical-scavenging activity.[1)] A related Brazilian Olacaceous plant, *Ptychopetalum olacoides*, is called Muira Puama, and used as a tonic and an aphrodisiac. Isolation of clerodane diterpenoids from *P. olacoides* and their NGF-potentiating activity were reported.[2)] Nothing was reported until our investigation of the leaves of *S. jasminodora*, constituents of its branches being reported.

From the branches of *S. jasminodora*, eight new dihydrochalcone, flavanone and flavone *C*-glycosides and *O*-glycosides, named schoepfiajasmin A–H (**1**–**8**), were isolated (Fig. 1), along with 14 known compounds, pentyl *O*-*β*-(2′-*O*-*β*-D-glucopyranosyl)-D-glucopyranoside (**9**),[3)] benzyl *O*-*β*-(6′-*O*-*β*-D-apiofuranosyl)-D-glucopyranoside (**10**),[4)] zizybeoside (**11**),[5,6)] vanilloloside (**12**),[7)] *β*-hydroxypropiovanillone 3-*O*-*β*-D-glucopyranoside (**13**),[8)] syringin (**14**),[9)] syringaresinol 4′-*O*-*β*-D-glucopyranoside (**15**),[10)] schoepfins B (**16**) and C (**17**),[11)] 2′,4,4′-trihydroxy-3′-*C*-glucopyranosyl chalcone (**18**),[12)] pinocembrin 7-*O*-glucopyranoside (**19**),[13)] (2*S*)-8-*C*-*β*-glucopyranosyl-7-hydroxyflavanone (**20**),[1)] isovitexin (**21**),[14)] and chrysin 7-*O*-*β*-D-glucopyranoside (**22**).[15)] The structures of the new compounds were elucidated by detailed examination of spectroscopic data and those of the known compounds were identified by comparison with reported data in the literature.

## Results and Discussion

From the 1-BuOH-soluble fraction of a MeOH extract of branches of *S. jasminodora*, chalcone and flavonoid glycosides were isolated by various kinds of chromatography. Their structures were elucidated from physico-chemical evidence.

Schoepfiajasmin A (**1**): $[\alpha]_D^{25}$ −19.7, was isolated as an amorphous powder and its elemental composition was determined to be $C_{26}H_{32}O_{12}$ by high-resolution (HR)-electrospray ionization (ESI)-mass spectrometry (MS). The IR spectrum exhibited absorptions attributable to hydroxy groups (3367 $cm^{-1}$), a carbonyl group and aromatic ring(s). The UV absorption bands also supported the presence of aromatic ring(s). The $^1$H-NMR spectrum exhibited signals for five intricately coupled and two *ortho*-coupled aromatic protons, anomeric protons [$\delta_H$ 4.72 (1H, d, $J$=9.6 Hz), 5.18 (1H, d, $J$=1.0 Hz)], two methylene protons [$\delta_H$ 2.96 (2H, t, $J$=7.2 Hz), 3.24 (2H, t, $J$=7.2 Hz)] coupled to each other and a highly deshielded hydroxy proton at $\delta_H$ 13.13. In the $^{13}$C-NMR spectrum, five typical signals [$\delta_C$ 109.0 (d), 76.4 (d), 78.9 (s), 73.6 (t), 64.7 (t)] assigned to those of a terminal apiofuranoside, and 13 $sp^2$ carbon and two methtylene signals together with six signals for a sugar moiety were observed (Table 1). Of the 13 $sp^2$ signals, one was assigned to a carbonyl functional group from its highly deshielded chemical shift ($\delta_C$ 203.9), the remaining 12 signals being expected to represent mono- (A ring) and tetrasubstituted (B ring) aromatic rings. In the heteronuclear multiple-bond correlation (HMBC) spectrum, one of the *ortho*-coupled aromatic protons ($\delta_H$ 7.73) showed a cross peak with the carbonyl carbon, and the $H_2$-*β* protons ($\delta_H$ 2.96) with the carbonyl carbon and aromatic carbon ($\delta_C$ 128.2), as well as $H_2$-*α* ($\delta_H$ 3.24) with C-1 ($\delta_C$ 141.0) (Fig. 2). Thus, the structure of the aglycone moiety was established to have a dihydrochalcone skeleton. The heteronuclear single quantum correlation spectrum (HSQC) between the anomeric proton ($\delta_H$ 4.72) and $\delta_C$ 72.0 indicated that shoepfijasmin A (**1**) is a 3′-*C*-glycoside, and the HMBC correlations between the anomeric proton and C-2′, 3′ and 4′ supported this assumption. On acid hydrolysis of **1**, schoepfin B (**16**)[11)] and D-apiose were obtained. The absolute configuration of apiose was determined by HPLC analysis with a chiral detector and the sugar linkage was determined to be on the hydroxy group at the C-2″ position from the HMBC correlation cross peak between the anomeric proton ($\delta_H$ 5.18) and C-2″ ($\delta_C$ 74.7). The absolute configuration of the 2-position of D-apiose must be *R* and judging from the small coupling constant of the anomeric proton ($J$=1.0 Hz), both oxygens at the 1‴- and 2‴-positions took up *quasi*-axial orientations, *i.e.*, *β*-D-apiofuranoside. Therefore, the structure of schoepfiajasmin A (**1**) was elucidated to be as shown in Fig. 1.

Schoepfiajasmin B (**2**): $[\alpha]_D^{25}$ −21.7, was isolated as an amorphous powder and its elemental composition was determined

The authors declare no conflict of interest.

* To whom correspondence should be addressed. e-mail: hotsuka@hiroshima-u.ac.jp

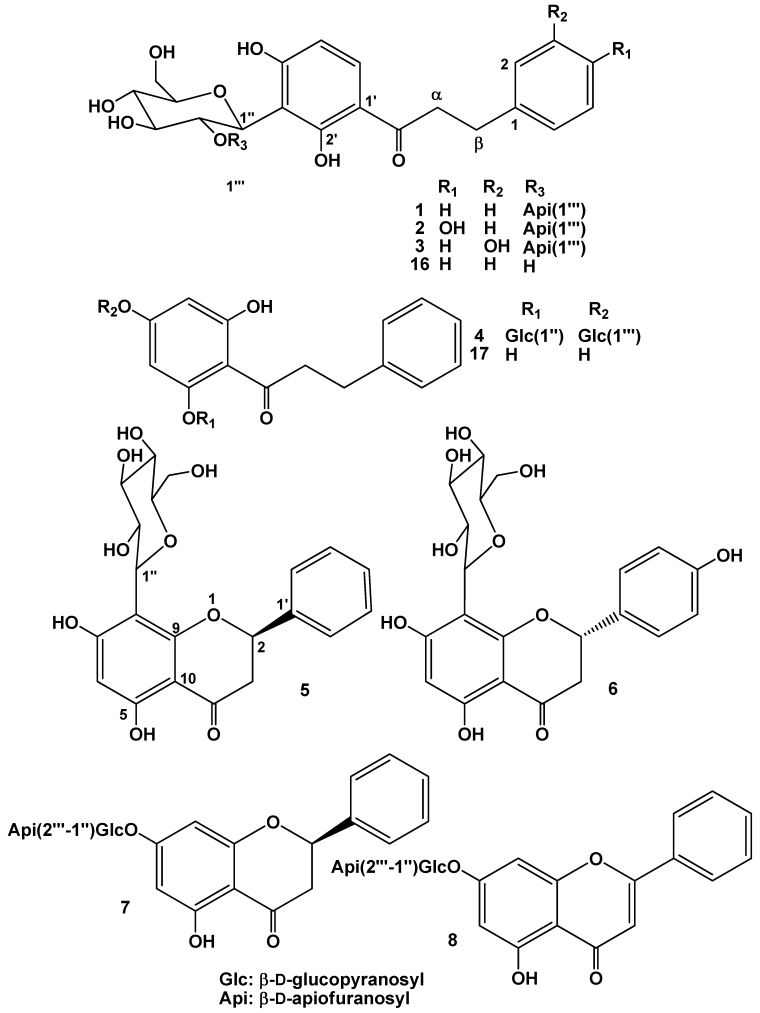


Fig. 1. Structures of Schoepfiajasmins A–H (**1**–**8**) and Schoepfin B (**16**)

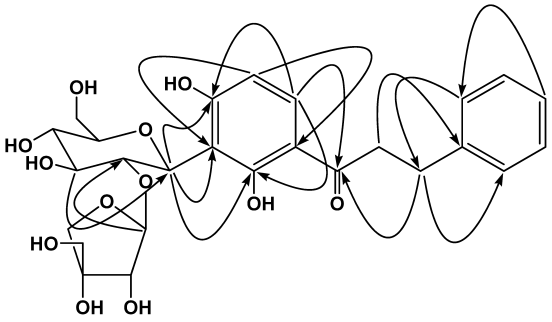

Fig. 2. HMBC Correlations for Schoepfiajasmin A (**1**)
Arrowheads denote C and arrow tails H.

to be $C_{26}H_{32}O_{13}$ by HR-ESI-MS. The spectroscopic data were similar to those of **1** and the monosubstituted aromatic ring must be replaced by a *para*-subsittuted one with an oxygen atom ($\delta_C$ 130.8, 128.7×2, 114.9×2, 155.2). Therefore, the structure of **2** was determined to be as shown in Fig. 1.

Schoepfiajasmin C (**3**): $[\alpha]_D^{26}$ −32.6, was also isolated as an amorphous powder and its elemental composition determined by HR-ESI-MS was the same as that of **2**. Spectroscopic data indicated that schoepfiajasmin C (**3**) was an analogous compound to **1** and **2**. Since the $^{13}$C-NMR data for the sugar moiety, and the B ring region together with two methylenes were essentially superimposable on those of **1** and **2** (Table 1), some modification had occurred in the disubstituted A ring. The A ring was not symmetrically substituted and thus the phenolic alcohol functional group was placed on the rare 3-position from the HMBC correlations from $H_2$-$\beta$ ($\delta_H$ 2.94) to C-2 ($\delta_C$ 116.3) with $\delta_H$ 6.68 (1H, d, $J$=2.4 Hz) and C-6 ($\delta_C$ 120.7) with $\delta_H$ 6.70 (1H, dd, $J$=7.9, 2.4 Hz) (Fig. 3). Therefore, the structure of schoepfiajasmin C (**3**) was elucidated to be as shown in Fig. 1.

Schoepfiajasmin D (**4**): $[\alpha]_D^{22}$ −86.0, was isolated as an amorphous powder and its elemental composition was determined to be $C_{27}H_{34}O_{14}$ by HR-ESI-MS. The NMR spectroscopic data indicated the presence of a monosubstituted benzene ring (C-1 to C-6) (A ring), which was seen in **1**, and two aromatic protons on the B ring were coupled in a *meta* relationship. Twelve $^{13}$C-NMR signals assignable to two sets of terminal glucopyranosides were also observed (1: $\delta_C$ 99.8, 101.6, 2: $\delta_C$ 73.3, 73.4, 3: $\delta_C$ 77.2, 77.3, 5: $\delta_C$ 76.7, 76.9, and 6: $\delta_C$ 61.1, 61.2). In the acid hydrolyzate of **4**, D-glucose was identified as a sugar component on HPLC analysis using a chiral detector. The mode of sugar linkage was determined to be $\beta$, judging from their coupling constants of anomeric protons (7.4, 7.7 Hz). Since in the HMBC spectrum, both of the *meta*-coupled aromatic protons [$\delta_H$ 6.17 (1H, d, $J$=2.0 Hz), 6.39 (1H, d, $J$=2.0 Hz)] showed correlation cross peaks with C-1′ ($\delta_C$

Table 1. $^{13}$C-NMR Spectroscopic Data for Schoepfiajasmins A–D (**1**–**4**) and 2′,4′,6′-Trihydroxychalcone (**17**)

| C | **1**[a)] | **2**[a)] | **3**[b)] | **4**[c)] | **17**[d)] |
|---|---|---|---|---|---|
| 1 | 141.0 | 130.8 | 144.0 (142.4)[c)] | 141.4 | 141.2 |
| 2 | 128.2 | 128.7 | 116.3 (113.1) | 128.1 | 127.7 |
| 3 | 128.2 | 114.9 | 158.5 (157.4) | 128.2 | 127.7 |
| 4 | 125.9 | 155.2 | 114.1 (112.1) | 125.6 | 125.2 |
| 5 | 128.2 | 114.9 | 130.5 (129.1) | 128.2 | 127.7 |
| 6 | 128.2 | 128.7 | 120.7 (118.9) | 128.1 | 127.7 |
| *α* | 38.6 | 38.8 | 40.4 (38.6) | 44.6 | 44.4 |
| *β* | 30.2 | 29.2 | 31.7 (30.3) | 29.7 | 29.6 |
| C=O | 203.9 | 203.9 | 205.8 (nd) | 203.5 | 203.3 |
| 1′ | 112.1 | 111.7 | 113.0 (112.0) | 108.2 | 103.1 |
| 2′ | 163.6 | 163.2 | 165.4 (nd) | 159.8 | 163.6 |
| 3′ | 112.3 | 111.9 | 114.0 (112.0) | 95.0 | 94.1 |
| 4′ | 163.6 | 163.2 | 165.4 (nd) | 161.5 | 164.0 |
| 5′ | 108.2 | 107.9 | 110.0 (108.5) | 98.1 | 163.6 |
| 6′ | 131.8 | 131.4 | 133.3 (131.6) | 162.7 | 94.1 |
| 1″ | 72.0 | 71.6 | 74.0 (72.0) | 101.0 | |
| 2″ | 74.7 | 74.5 | 76.5 (74.7) | 73.3 | |
| 3″ | 79.3 | 78.9 | 80.9 (79.2) | 77.3 | |
| 4″ | 70.8 | 70.4 | 71.8 (70.8) | 70.1 | |
| 5″ | 81.1 | 80.7 | 80.6 (81.1) | 76.7 | |
| 6″ | 61.4 | 61.1 | 62.8 (61.4) | 61.1 | |
| 1‴ | 109.0 | 108.7 | 110.9 (108.9) | 99.8 | |
| 2‴ | 76.4 | 76.2 | 78.1 (76.5) | 73.4 | |
| 3‴ | 78.9 | 78.6 | 80.6 (78.9) | 77.2 | |
| 4‴ | 73.6 | 73.2 | 75.1 (73.6) | 70.2 | |
| 5‴ | 64.7 | 64.4 | 66.3 (64.7) | 76.9 | |
| 6‴ | | | | 61.2 | |

*a*) Data for DMSO-$d_6$ at 95°C and 150 MHz. *b*) Data for $CD_3OD$ at 35°C and 100 MHz. *c*) Data for DMSO-$d_6$ at 95°C and 100 MHz. *d*) Data for $(CD_3)_2CO$ at 150 MHz.[16] nd: not detected.

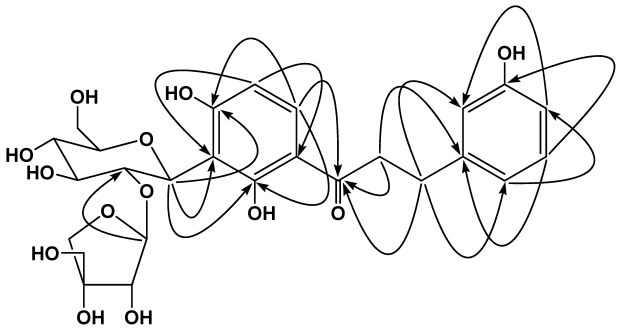


Fig. 3. HMBC Correlations for Schoepfiajasmin C (**3**)

Arrowheads denote C and arrow tails H.

108.2), the substitution pattern in the B ring was expected to be a 2,4,6- or 3,4,5-trihydroxy symmetrical system and the asymmetry in the B ring was induced by 2,4- or 3,4-di-*O*-*β*-D-glucopyranosylation, respectively. From biosynthetic point of view, 2,4,6-substitution was more plausible, and the high field shifts of the C-1′, C-3′ and C-5′ signals in the $^{13}$C-NMR spectrum supported this fact. The reported spectroscopic data for its aglycone (**17**) further supported the substitution pattern.[16] Therefore, the structure of schoepfiajasmin D (**4**) was elucidated to be 2′,4′,6′-trihydroxydihydrochalcone 2′,4′-di-*O*-*β*-D-glucopyranoside, as shown in Fig. 1.

Schoepfiajasmin E (**5**): $[\alpha]_D^{26}$ +45.7, was isolated as an amorphous powder and its elemental composition was determined to be $C_{21}H_{22}O_8$ by HR-ESI-MS. The IR spectrum exhibited absorption bands attributable to a hydroxy group (3441 cm$^{-1}$), a ketone functional group (1674 cm$^{-1}$), and an aromatic ring(s) (1594 cm$^{-1}$), and the UV absorptions were also consistent with the presence of an aromatic ring(s). The $^{13}$C-NMR spectrum exhibited 13 $sp^2$ signals, which comprised those of one carbonyl carbon and two aromatic rings. One methylene, one oxygenated methine and six signals assignable to a *C*-glucosyl moiety were also observed (Table 2). In the $^1$H-NMR spectrum, two aromatic signals were coupled in an *ortho* relationship and five aromatic signals were expected be on one aromatic ring (Table 2). One ($\delta_H$ 7.73) of the *ortho* coupled aromatic protons showed a correlation cross peak with the carbonyl carbon ($\delta_C$ 193.5) in the HMBC spectrum, thus the *ortho*-coupled aromatic protons were placed at the H-5 and H-6 positions, and further correlations between H-2 ($\delta_H$ 5.51) and C-2′ ($\delta_C$ 127.3), and $H_2$-3 ($\delta_H$ 2.84, 3.00) and the carbonyl carbon and C-1′ ($\delta_C$ 140.6) were observed. A crucial HMBC correlation from H-2 to C-9 established the flavanone skeleton. The position of *C*-glucosylation was determined to be at C-8 from the HMBC correlations from the anomeric proton to C-7, C-8 and C-9. Therefore, the C-7 position carried a hydroxy group judging from its deshielded chemical shift ($\delta_C$ 165.4) and the structure was elucidated to be as shown in Fig. 1. The absolute configuration at the C-2 position was determined to be *R* from the positive and negative Cotton effects at 301 nm and 334 nm, respectively, in the circular dichroism (CD) spectrum.[17,18]

Schoepfiajasmin F (**6**): $[\alpha]_D^{25}$ +28.0, was isolated as an amorphous powder and its elemental composition was determined to be $C_{21}H_{22}O_9$ by HR-ESI-MS. The spectroscopic data indi-

Table 2. $^{13}$C-NMR Spectroscopic Data for Schoepfiajasmins E–H (**5**–**8**)

| C | **5**[a)] | **6**[b)] | **7**[c)] | **8**[c)] |
|---|---|---|---|---|
| 2 | 80.8 | 80.9 | 78.6 | 163.7 |
| 3 | 45.4 | 45.2 | 42.1 | 105.6 |
| 4 | 193.5 | 193.9 | 196.7 | 182.1 |
| 5 | 129.5 | 129.4 | 162.9 | 161.1 |
| 6 | 112.1 | 112.0 | 96.5 | 99.5 |
| 7 | 165.4 | 165.4 | 164.9 | 163.7 |
| 8 | 113.5 | 113.5 | 95.4 | 94.9 |
| 9 | 163.9 | 164.1 | 162.5 | 157.0 |
| 10 | 115.5 | 115.5 | 103.3 | 105.4 |
| 1′ | 140.6 | 131.7 | 138.4 | 130.5 |
| 2′ | 127.3 | 129.0 | 126.7 | 126.4 |
| 3′ | 129.6 | 116.3 | 128.5 | 129.1 |
| 4′ | 129.4 | 158.8 | 128.6 | 132.1 |
| 5′ | 129.6 | 116.3 | 128.5 | 129.1 |
| 6′ | 127.3 | 129.0 | 126.7 | 126.4 |
| 1″ | 75.9 | 75.9 | 97.7 | 98.1 |
| 2″ | 72.9 | 72.8 | 75.7 | 75.8 |
| 3″ | 80.0 | 80.0 | 76.7 | 76.7 |
| 4″ | 71.8 | 71.9 | 69.7 | 69.8 |
| 5″ | 82.5 | 85.2 | 76.9 | 76.7 |
| 6‴ | 62.9 | 63.0 | 60.5 | 60.5 |
| 1‴ | | | 108.7 | 108.7 |
| 2‴ | | | 76.0 | 76.0 |
| 3‴ | | | 79.2 | 79.2 |
| 4‴ | | | 73.9 | 73.9 |
| 5‴ | | | 64.2 | 64.1 |

*a*) Data for $CD_3OD$ at 35°C and 100 MHz. *b*) Data for $CD_3OD$ at 35°C and 150 MHz. *c*) Data for DMSO-$d_6$ at 35°C and 150 MHz.

cated that schoepfiajasmin F (**6**) was a similar compound to **5** and the 4′-position of the B-ring was substituted by a hydroxy group ($\delta_C$ 158.8). The absolute configuration at the C-2 position was determined to be *S* from the negative and positive Cotton effects at 304 nm and 337 nm, respectively, in the CD spectrum.

Schoepfiajasmin G (**7**): $[\alpha]_D^{25}$ −120, was isolated as an amorphous powder and its elemental composition was determined to be $C_{26}H_{30}O_{13}$ by HR-ESI-MS. The spectroscopic data indicated **7** was a congeneric compound to **5**. A highly deshileded chelated hydroxy proton was observed at $\delta_H$ 11.91 in the $^1$H-NMR spectrum and two aromatic protons on the A-ring were coupled to each other in a *meta* relationship. The anomeric carbon chemical shift ($\delta_C$ 97.7) of the glucopyranose moiety indicated that this sugar was not directly connected to a carbon atom, but through an oxygen atom. HMBC correlations H-1″ ($\delta_H$ 5.08) to C-7 ($\delta_C$ 164.9) and H-1‴ ($\delta_H$ 5.31) to C-2″ ($\delta_C$ 75.7) confirmed the positions of sugar linkages to the aglycone and the terminal apiofuranose to the inner sugar. Therefore, the structure of **7** was elucidated to be as shown in Fig. 1. The absolute configuration at the C-2 position was determined to be *R* from the positive and negative Cotton effects at 279 nm and 333 nm, respectively, in the CD spectrum.[17,18)]

Schoepfiajasmin H (**8**): $[\alpha]_D^{22}$ −75.0, was isolated as a pale yellow amorphous powder and its elemental composition was determined to be $C_{26}H_{28}O_{13}$ by HR-ESI-MS, which was two mass units less than that of **7**. In the $^{13}$C-NMR spectrum, the signals for oxygenated methine and methylene carbons, which were observed in **7**, were replaced by a trisubstituted double bond [$\delta_C$ 105.6 (d), 163.7 (s)], and the oxygenated methine and methylene protons observed in the $^1$H-NMR spectrum were replaced by an olefinic proton at $\delta_H$ 7.04. Thus, **8** was expected to have a flavone skeleton and its structure is as shown in Fig. 1.

From the branches of *S. jasminodora*, three relatively rare dihydrochacone *C*-glycosides (**1**–**3**) and di-*O*-glucopyranoside (**4**) were isolated. Shoepfiajasmin C (**3**) possesses only one hydroxy functional group at the C-3 position on the benzene ring. This is a rare substitution pattern and is not frequently found as a natural product. When 3-hydroxycinnamic acid was fed to metabolically engineered yeast, the isolation of 3-hydroxydihydrochalcone was reported.[19)]

## Experimental

**General Experimental Procedures** Optical rotations were measured on a JASCO P-1030 digital polarimeter. IR and UV spectra were measured on Horiba FT-710 and JASCO V-520 UV/Vis spectrophotometers, respectively. $^1$H- and $^{13}$C-NMR spectra were taken on a JEOL JNM $\alpha$-400 spectrometer at 400 MHz and 100 MHz, respectively, with tetramethylsilane as an internal standard. CD spectra were measured with a JASCO J-720 spectropolarimeter. Positive-ion HR-ESI-MS was performed with an Applied Biosystems QSTAR XL NanoSpray™ System.

A highly-porous synthetic resin (Diaion HP-20) was purchased from Mitsubishi Kagaku (Tokyo, Japan). Silica gel CC was performed on silica gel 60 (E. Merck, Darmstadt, Germany), and ODS open CC on Cosmosil 75$C_{18}$-OPN (Nacalai Tesque, Kyoto, Japan) [$\Phi$=45 mm, $L$=25 cm; $H_2O$–MeOH (9 : 1, 1 L)→(1 : 9, 1 L), linear gradient, 10 g fractions being collected]. The DCCC (Tokyo Rikakikai, Tokyo, Japan) was equipped with 500 glass columns ($\Phi$=2 mm, $L$=40 cm), the lower and upper layers of a solvent mixture of $CHCl_3$–MeOH–$H_2O$–1-PrOH (9 : 12 : 8 : 2) being used as the stationary and mobile phases, respectively. Five-gram fractions were collected and numbered according to their order of elution with the mobile phase. HPLC was performed on an ODS column (Inertsil; ODS-3, GL Science, Tokyo, Japan; $\Phi$=6 mm, $L$=250 mm, 1.6 mL/min), and the eluate was monitored with a UV detector at 254 nm, and a refractive index monitor.

**Plant Material** Branches of *S. jasminodora* were collected in Kunigami Village, Kunigami County, Okinawa, Japan, in July 2006, and a voucher specimen was deposited in the Herbarium of the Faculty of Pharmaceutical Sciences, Graduate School of Biomedical and Health Science, Hiroshima University (06-SJ-Okinawa-0704).

**Extraction and Isolation** Branches of *S. jasminodora* (13.5 kg) were extracted three times with MeOH (45 L×3) at room temperature for one week and then concentrated to 3 L *in vacuo*. The concentrated extract was washed with *n*-hexane (3 L, 35.5 g), and then the MeOH layer was concentrated to a gummy mass. The latter was suspended in water (3 L) and then extracted with EtOAc (3 L) to give 53.2 g of an EtOAc-soluble fraction. The aqueous layer was extracted with 1-BuOH (3 L) to give a 1-BuOH-soluble fraction (146 g), and the remaining water-layer was concentrated to furnish 28.9 g of a water-soluble fraction. The 1-BuOH-soluble fraction (145 g) was subjected to Diaion HP-20 CC ($\Phi$=50 mm, $L$=50 cm), using a solvent system of $H_2O$–MeOH [(4 : 1, 6 L), (3 : 2, 6 L), (2 : 3, 6 L), and (1 : 4, 6 L)], and MeOH, 1 L fractions being collected. The residue (9.11 g) in fractions 4–8

was subjected to silica gel CC ($\Phi$=3.6 cm, $L$=40 cm), using $CHCl_3$ (1.5 L), $CHCl_3$–MeOH [(49 : 1, 1.5 L), (24 : 1, 1.5 L), (23 : 2, 1.5 L), (9 : 1, 3 L), (17 : 3, 1.5 L), (4 : 1, 1.5 L), (3 : 1, 1.5 L), and (7 : 3, 1.5 L) ], $CHCl_3$–MeOH–$H_2O$ (35 : 15 : 2, 1.5 L), and MeOH (1.5 L), 250 mL fractions being collected. The residue (3.34 g) in fractions was separated by ODS open CC and then the residue (581 mg) in fractions 63–90 was purified by DCCC. The residue (202 mg) in fractions 37–48 was finally purified by HPLC ($H_2O$–MeOH, 4 : 1) to give 11.8 mg of **14**, 2.02 mg of **13**, 21.3 mg of **10** and 2.54 mg of **9** from the peaks at 19 min, 22 min, 29 min and 32 min, respectively. The residue (1.09 g) in fractions 43–53 obtained on silica gel CC was separated by ODS open CC and the residue (20.0 mg) in fractions 31–35 was purified by DCCC to give 10.1 mg of **12** in fractions 71–86. The residue (132 mg) in fractions 60–74 was purified by DCCC and the precipitate (8.23 mg) in fractions 33–38 was purified by HPLC ($H_2O$–MeOH, 4 : 1) to give 2.82 mg of **11** from the peak at 14 min.

The residue (14.7 g) in fractions 9–13 obtained on Diaion HP-20 CC was subjected to silica gel CC ($\Phi$=5.5 cm, $L$=46 cm), using $CHCl_3$ (3 L), $CHCl_3$–MeOH [(49 : 1, 3 L), (24 : 1, 3 L), (23 : 2, 3 L), (9 : 1, 3 L), (17 : 3, 3 L), (4 : 1, 3 L), (3 : 1, 3 L), (7 : 3, 3 L) (3 : 2. 3 L), and (1 : 1, 3 L)], $CHCl_3$–MeOH–$H_2O$ (25 : 25 : 2, 3 L), and MeOH (3 L), 500 mL fractions being collected. The residue (2.91 g) in fractions 29–42 was separated by ODS open CC to give two residues, 539 mg in fractions 73–108 and 987 mg in fractions 125–164. The former residue was purified DCCC and the residue (70.0 mg) in fractions 57–62 was purified again by HPLC ($H_2O$–MeOH, 7 : 3) to give a residue (14.0 mg) from the peak at 12 min. The residue was further purified by HPLC (Cosmosil; Cholester, Nakalai Tesque, Kyoto, Japan; $\Phi$=10 mm, $L$=250 mm, 1.6 mL/min) ($H_2O$–MeOH, 7 : 3) to give 1.0 mg of **6** from the peak at 35 min. The latter residue was separated by DCCC and the residue (271 mg) was purified by HPLC ($H_2O$–MeOH, 3 : 2) to afford 34.1 mg of **5** and 27.4 mg of **20** from the peaks at 12 min and 14 min, respectively. The residue (3.20 g) in fractions 43–53 was separated by ODS open CC and the residue (184 mg) in fractions 71–76 was purified by DCCC. The residue (129 mg) in fractions 25–36 was finally purified by HPLC ($H_2O$–MeOH, 7 : 3) to afford 29.1 mg of **2** from the peak at 52 min. The residue (2.58 g) in fractions 54–68 was separated by ODS open CC and the residue (215 mg) in fractions 77–95 was purified by DCCC. The residue (30.2 mg) in fractions 59–66 was finally purified by HPLC to yield 8.19 mg of **21** from the peak at 44 min. The residue (2.58 g) in fractions 54–57 was separated by ODS open CC and the residue (133 mg) in fractions 174–190 was purified by DCCC. The residue (19.7 mg) in fractions 24–28 was finally purified by HPLC ($H_2O$–MeOH, 3 : 2) to give 4.05 mg of **3** from the peak at 16 min.

The residue (10.5 g) in fractions 14–16 obtained on Diaion HP-20 CC was subjected to silica gel CC ($\Phi$=3.6 cm, $L$=50 cm), using $CHCl_3$ (1.5 L), $CHCl_3$–MeOH [(49 : 1, 1.5 L), (24 : 1, 1.5 L), (23 : 2, 1.5 L), (9 : 1, 3 L), (17 : 3, 1.5 L), (4 : 1, 1.5 L), (3 : 1, 1.5 L), and (7 : 3, 1.5 L)], $CHCl_3$–MeOH–$H_2O$ (35 : 15 : 2, 1.5 L), and MeOH (1.5 L), 250 mL fractions being collected. The residue (743 mg) in fractions 24–33 was separated by ODS open CC and the residue (230 mg) in fractions 127–138 was subjected to DCCC. The residue (70 mg) in fractions 35–40 was purified by HPLC ($H_2O$–MeOH, 13 : 7) to give 28.5 mg of **15** from the peak at 26 min. The residue (1.97 g) in fractions 34–44 was separated by ODS open CC and the residue (404 mg) in fractions 102–114 was subjected to DCCC to give 20.2 mg of **18** in fractions 50–59. The residue (2.60 g) in fractions 45–57 was separated by ODS open CC and the residue (249 mg) in fractions 199–206 was purified by DCCC. The residue (29.8 mg) in fractions 40–63 was finally purified by HPLC ($H_2O$–MeOH, 3 : 2) to afford 2.01 mg of **4** from the peak at 32 min.

The residue (10.5 g) in fractions 17–20 obtained on Diaion HP-20 CC was subjected to silica gel CC ($\Phi$=3.6 cm, $L$=40 cm), using $CHCl_3$ (1.5 L), $CHCl_3$–MeOH [(49 : 1, 1.5 L), (24 : 1, 1.5 L), (23 : 2, 1.5 L), (9 : 1, 3 L), (17 : 3, 1.5 L), (4 : 1, 1.5 L), (3 : 1, 1.5 L), and (7 : 3, 1.5 L)], $CHCl_3$–MeOH–$H_2O$ (35 : 15 : 2, 1.5 L), and MeOH (1.5 L), 250 mL fractions being collected. The soluble residue (1.51 g) in fractions 26–36 was separated by ODS Open CC and the residue (880 mg) was purified by DCCC. The residue (50 mg out of 147 mg) in fractions 117–144 was finally purified by HPLC to give 11.2 mg of **16** and 4.58 mg of **17** from the peaks at 41 min and 49 min, respectively. The precipitate (100 mg out of 687 mg) obtained in fractions 26–36 was purified by HPLC ($H_2O$–MeOH, 3 : 2) to give 26.3 mg of **19** and 3.00 mg of **22** from the peaks at 34 min and 42 min, respectively. The residue (1.31 g) in fractions 37–46 was separated by ODS open CC, and the residue (127 mg) was subjected to DCCC to yield 42.9 mg of **1** and 23 mg of **7** in fractions 42–62 and 65–82, respectively. The residue (168 mg) in fractions 211–220 was separated by DCCC and the residue (22.3 mg) in fractions 120–143 was purified by HPLC ($H_2O$–MeOH, 11 : 9) to afford 2.40 mg of **9** from the peak at 25 min.

Schoepfiajasmin A (**1**): Amorphous powder, $[\alpha]_D^{25}$ −19.7 ($c$=0.99, MeOH); IR $\nu_{max}$ (film) $cm^{-1}$: 3367, 2932, 1619, 1499, 1446, 1261, 1078, 821; UV $\lambda_{max}$ (MeOH) nm (log$\varepsilon$): 319 (3.81), 278 (3.96), 217 (4.14); $^1$H-NMR (600 MHz, DMSO-$d_6$, 95°C) $\delta$: 13.13 (1H, s, 2′-OH), 7.73 (1H, d, $J$=8.9 Hz, H-6′), 7.26 (4H, m, $J$=5.8 Hz, H-2, 3, 5, 6), 7.16 (1H, tt, $J$=5.8, 2.8 Hz, H-4), 6.39 (1H, d, $J$=8.9 Hz, H-5′), 5.18 (1H, d, $J$=1.0 Hz, H-1‴), 4.72 (1H, d, $J$=9.6 Hz, H-1″), 4.14 (1H, brt, $J$=9.0 Hz, H-2″), 3.68 (1H, dd, $J$=11.7, 2.4 Hz, H-6″a), 3.58 (1H, d, $J$=1.0 Hz, H-2‴), 3.49 (1H, dd, $J$=11.7, 5.5 Hz, H-6″b), 3.43 (1H, dd, $J$=8.6, 8.6 Hz, H-3″), 3.25 (1H, dd, $J$=8.9, 8.6 Hz, H-4″), 3.24 (2H, t, $J$=7.2 Hz, $H_2$-$\alpha$), 3.21 (1H, ddd, $J$=8.9, 5.5, 2.4 Hz, H-5″), 3.15 (1H, d, $J$=11.3 Hz, H-5‴a), 3.12 (1H, d, $J$=9.3 Hz, H-4‴a), 3.01 (1H, d, $J$=11.3 Hz, H-5‴b), 2.96 (2H, t, $J$=7.2 Hz, $H_2$-$\beta$), 2.62 (1H, d, $J$=9.3 Hz, H-4‴b); $^{13}$C-NMR (150 MHz, DMSO-$d_6$, 95°C): Table 1; HR-ESI-MS (positive-ion mode) $m/z$: 559.1785 $[M+Na]^+$ (Calcd for $C_{26}H_{32}O_{12}Na$: 559.1786).

Schoepfiajasmin B (**2**): Amorphous powder, $[\alpha]_D^{25}$ −21.7 ($c$=1.04, MeOH); IR $\nu_{max}$ (film) $cm^{-1}$: 3356, 2934, 1615, 1513, 1446, 1362, 1257, 1081, 998, 825; UV $\lambda_{max}$ (MeOH) nm (log$\varepsilon$): 317 (3.72), 276 (3.90), 217 (4.07); $^1$H-NMR (600 MHz, DMSO-$d_6$, 95°C) $\delta$: 13.15 (1H, s, 2′-OH), 8.82 (1H, s, 4-OH), 7.70 (1H, d, $J$=8.9 Hz, H-6′), 7.02 (2H, d, $J$=8.3 Hz, H-2, 6), 6.66 (2H, d, $J$=8.3 Hz, H-3, 5), 6.38 (1H, d, $J$=8.9 Hz, H-5′), 5.17 (1H, brs, H-1‴), 4.73 (1H, d, $J$=9.6 Hz, H-1″), 4.10 (1H, m, H-2″), 3.68 (1H, dd, $J$=11.7, 2.1 Hz, H-6″a), 3.59 (1H, brs, H-2‴), 3.50 (1H, dd, $J$=11.7, 5.5 Hz, H-6″b), 3.43 (1H, dd, $J$=8.9, 8.9 Hz, H-3″), 3.26 (1H, dd, $J$=8.9, 8.9 Hz, H-4″), 3.21 (1H, ddd, $J$=8.9, 5.5, 2.1 Hz, H-5″), 3.13 (2H, t, $J$=7.2 Hz, $H_2$-$\alpha$), 3.16 (1H, d, $J$=11.0 Hz, H-5‴a), 3.12 (1H, d, $J$=9.3 Hz, H-4‴a), 3.04

(1H, d, $J$=11.0 Hz, H-5‴b), 2.84 (2H, t, $J$=6.8 Hz, $H_2$-$\beta$), 2.64 (1H, d, $J$=9.3 Hz, H-4‴b); $^{13}$C-NMR (150 MHz, DMSO-$d_6$, 95°C): Table 1; HR-ESI-MS (positive-ion mode) $m/z$: 575.1729 $[M+Na]^+$ (Calcd for $C_{26}H_{32}O_{13}Na$: 575.1735).

Schoepfiajasmin C (**3**): Amorphous powder, $[\alpha]_D^{26}$ −32.6 ($c$=0.23, MeOH); IR $\nu_{max}$ (film) cm$^{-1}$: 3394, 2930, 1618, 1502, 1454, 1360, 1272, 1079, 1023, 899; UV $\lambda_{max}$ (MeOH) nm (log$\varepsilon$): 316 (3.85), 277 (4.03), 218 (4.14); $^1$H-NMR (400 MHz, $CD_3OD$, 35°C) $\delta$: 7.72 (1H, d, $J$=8.8 Hz, H-6′), 7.06 (1H, dd, $J$=7.9, 7.9 Hz, H-5), 6.70 (1H, dd-like, $J$=7.9, 2.4 Hz, H-6), 6.68 (1H, t-like, $J$=2.4 Hz, H-2), 6.59 (1H, ddd, $J$=7.9, 2.4, 2.4 Hz, H-4), 6.40 (1H, d, $J$=8.8 Hz, H-5′), 5.30 (1H, d, $J$=0.7 Hz, H-1‴), 4.92 (1H, d, $J$=9.0 Hz, H-1″), 4.48 (1H, m, H-2″), 3.85 (1H, dd, $J$=12.0, 2.0 Hz, H-6″a), 3.76 (1H, d, $J$=0.7 Hz, H-2‴), 3.70 (1H, dd, $J$=12.0, 4.9 Hz, H-6″b), 3.58 (1H, dd, $J$=9.2, 9.2 Hz, H-3″), 3.45 (1H, dd, $J$=9.7, 9.2 Hz, H-4″), 3.36 (1H, d, $J$=11.1 Hz, H-5‴a), 3.35 (1H, ddd, $J$=9.7, 4.9, 2.0 Hz, H-5″), 3.22 (2H, t, $J$=7.8 Hz, $H_2$-$\alpha$), 3.17 (1H, d, $J$=11.1 Hz, H-5‴b), 3.15 (1H, d, $J$=9.6 Hz, H-4‴a), 2.94 (2H, t, $J$=7.8 Hz, $H_2$-$\beta$), 2.58 (1H, d, $J$=9.6 Hz, H-4‴b); $^{13}$C-NMR (100 MHz, $CD_3OD$, 35°C): Table 1; HR-ESI-MS (positive-ion mode) $m/z$: 575.1733 $[M+Na]^+$ (Calcd for $C_{26}H_{32}O_{13}Na$: 575.1735).

Schoepfiajasmin D (**4**): Amorphous powder, $[\alpha]_D^{22}$ −86.0 ($c$=0.10, MeOH); IR $\nu_{max}$ (film) cm$^{-1}$: 3356, 2923, 1622, 1493, 1431, 1370, 1275, 1177, 1075, 829; UV $\lambda_{max}$ (MeOH) nm (log$\varepsilon$): 307 (3.97), 275 (4.30), 221 (4.29); $^1$H-NMR (400 MHz, DMSO-$d_6$, 95°C) $\delta$: 7.23 (4H, m, H-2, 3, 5, 6), 7.14 (1H, m, H-4), 6.39 (1H, d, $J$=2.0 Hz, H-3′), 6.17 (1H, d, $J$=2.0 Hz, H-5′), 5.00 (1H, d, $J$=7.7 Hz, H-1″), 4.94 (1H, d, $J$=7.4 Hz, H-1‴), 3.70 (1H, dd, $J$=11.7, 2.0 Hz, H-6″a), 3.70 (1H, dd, $J$=11.8, 1.9 Hz, H-6‴a), 3.50 (1H, dd, $J$=11.7, 6.5 Hz, H-6″b), 3.50 (1H, dd, $J$=11.8, 6.4 Hz, H-6‴b), 3.45 (2H, t, $J$=7.4 Hz, $H_2$-$\alpha$), 3.42 (1H, brt, $J$=9.0 Hz, H-3″), 3.42 (1H, brt, $J$=9.0 Hz, H-3‴), 3.32 (4H, m, H-2”, 5”, 2‴, 5‴), 3.18 (2H, m, H-4″, 4‴), 2.93 (2H, t, $J$=7.4 Hz, $H_2$-$\beta$); $^{13}$C-NMR (100 MHz, DMSO-$d_6$, 95°C): Table 1; HR-ESI-MS (positive-ion mode) $m/z$: 605.1847 $[M+Na]^+$ (Calcd for $C_{27}H_{34}O_{14}Na$: 605.1841).

Schoepfiajasmin E (**5**): Amorphous powder, $[\alpha]_D^{26}$ +45.7 ($c$=1.91, MeOH); IR $\nu_{max}$ (film) cm$^{-1}$: 3441, 2933, 1674, 1594, 1448, 1366, 1266, 1109, 1022, 891; UV $\lambda_{max}$ (MeOH) nm (log$\varepsilon$): 310 (3.85), 278 (4.02), 216 (4.22); $^1$H-NMR (400 MHz, $CD_3OD$, 95°C) $\delta$: 7.73 (1H, d, $J$=8.6 Hz, H-5), 7.54 (2H, dd, $J$=7.0, 1.4 Hz, H-2′, 6′), 7.41 (2H, dd, $J$=7.3, 7.0 Hz, H-3′, 5′), 7.34 (1H, tt, $J$=7.3, 1.4 Hz, H-4′), 6.57 (1H, d, $J$=8.6 Hz, H-6), 5.51 (1H, dd, $J$=12.8, 3.1 Hz, H-2), 4.92 (1H, d, $J$=9.5 Hz, H-1″), 4.08 (1H, brdd, $J$=9.5, 9.5 Hz, H-2″), 3.86 (1H, dd, $J$=11.7, 1.7 Hz, H-6″a), 3.83 (1H, ddd, $J$=9.0, 4.5, 1.7 Hz, H-5″), 3.67 (1H, dd, $J$=11.7, 4.5 Hz, H-6″b), 3.40 (1H, dd, $J$=9.5, 9.0 Hz, H-3″), 3.34 (1H, brt, $J$=9.0 Hz, H-4″), 3.00 (1H, dd, $J$=16.8, 3.1 Hz. H-3eq), 2.84 (1H, dd, $J$=16.8, 12.8 Hz, H-3ax); $^{13}$C-NMR (100 MHz, $CD_3OD$, 35°C): Table 2; CD $\Delta\varepsilon$ (nm): −0.86 (334), +3.05 (301) ($c$=2.70×10$^{-5}$ M, MeOH); HR-ESI-MS (positive-ion mode) $m/z$: 425.1207 $[M+Na]^+$ (Calcd for $C_{21}H_{22}O_8Na$: 425.1207).

Schoepfiajasmin F (**6**): Amorphous powder, $[\alpha]_D^{25}$ +28.0 ($c$=0.10, MeOH); IR $\nu_{max}$ (film) cm$^{-1}$: 3449, 2922, 1637, 1559, 1450, 1359, 1262, 1074, 835; UV $\lambda_{max}$ (MeOH) nm (log$\varepsilon$): 312 (3.92), 274 (4.13), 229 (4.40); $^1$H-NMR (600 MHz, $CD_3OD$, 35°C) $\delta$: 7.71 (1H, d, $J$=8.9 Hz, H-5), 7.40 (2H, d, $J$=8.5 Hz, H-2′, 6′), 6.81 (2H, d, $J$=8.5 Hz, H-3′, 5′), 6.51 (1H, d, $J$=8.9 Hz, H-6), 5.43 (1H, dd, $J$=12.5, 3.0 Hz, H-2), 4.90 (1H, d, $J$=9.8 Hz, H-1′), 4.07 (1H, dd, $J$=9.8, 8.7 Hz, H-2′), 3.82 (1H, dd, $J$=12.0, 1.6 Hz, H-6′a), 3.70 (1H, dd, $J$=12.0, 5.1 Hz, H-6′b), 3.41 (1H, dd, $J$=9.2, 8.7 Hz, H-3′), 3.36 (1H, ddd, $J$=9.1, 5.1, 1.6 Hz, H-5′), 3.34 (1H, brdd, $J$=9.0, 9.0 Hz, H-4′), 2.97 (1H, dd, $J$=16.9, 12.5 Hz, H-3a), 2.72 (1H, dd, $J$=16.9, 3.0 Hz, H-3b); $^{13}$C-NMR (150 MHz, $CD_3OD$, 35°C): Table 2; CD $\Delta\varepsilon$ (nm): +1.12 (337), −0.78 (304) ($c$=4.80×10$^{-5}$ M, MeOH); HR-ESI-MS (positive-ion mode) $m/z$: 441.1156 $[M+Na]^+$ (Calcd for $C_{21}H_{22}O_9Na$: 441.1156).

Schoepfiajasmin G (**7**): Amorphous powder, $[\alpha]_D^{25}$ −120 ($c$=0.02); IR $\nu_{max}$ (film) cm$^{-1}$: 3394, 2934, 1644, 1577, 1449, 1375, 1297, 1085, 1027, 829; UV $\lambda_{max}$ (MeOH) nm (log$\varepsilon$): 321 (3.66), 280 (4.09), 220 (4.17); $^1$H-NMR (600 MHz, DMSO-$d_6$, 35°C) $\delta$: 11.91 (1H, s, 5-OH), 7.52 (2H, d, $J$=7.5 Hz, H-2′, 6′), 7.41 (3H, m, H-3′, 4′, 5′), 6.18 (1H, d, $J$=2.1 Hz, H-8), 6.13 (1H, d, $J$=2.1 Hz, H-6), 5.63 (1H, dd, $J$=12.6, 2.9 Hz, H-2), 5.31 (1H, d, $J$=1.3 Hz, H-1‴), 5.08 (1H, d, $J$=7.1 Hz, H-1″), 3.85 (1H, d, $J$=9.5 Hz, H-4‴a), 3.77 (1H, d, $J$=1.3 Hz, H-2‴), 3.70 (1H, dd, $J$=12.0, 2.3 Hz, H-6″a), 3.62 (1H, d, $J$=9.5 Hz, H-4‴b), 3.49 (1H, dd, $J$=8.9, 7.1 Hz, H-2″), 3.45 (1H, dd, $J$=8.9, 8.5 Hz, H-3″), 3.48 (1H, dd, $J$=12.0, 5.2 Hz, H-6″b), 3.37 (1H, ddd, $J$=9.6, 5.2, 2.3 Hz, H-5″), 3.35 (1H, d, $J$=11.6 Hz, H-5‴a), 3.33 (1H, d, $J$=11.6 Hz, H-5‴b), 3.27 (1H, dd, $J$=17.2, 12.4 Hz, H-3ax), 3.23 (1H, dd, $J$=9.6, 8.5 Hz, H-4″), 2.84 (1H, dd, $J$=17.2, 2.9 Hz, H-3eq); $^{13}$C-NMR (150 MHz, DMSO-$d_6$, 35°C): Table 2; CD $\Delta\varepsilon$ (nm): −1.41 (333), +1.51 (279) ($c$=4.60×10$^{-5}$ M, MeOH); HR-ESI-MS (positive-ion mode) $m/z$: 573.1576 $[M+Na]^+$ (Calcd for $C_{26}H_{30}O_{13}Na$: 573.1579).

Schoepfiajasmin H (**8**): Pale yellow amorphous powder, $[\alpha]_D^{22}$ −75.0 ($c$=0.20, $C_5H_5N$); IR $\nu_{max}$ (film) cm$^{-1}$: 3395, 2928, 1664, 1613, 1452, 1349, 1302, 1077, 1041, 821; UV $\lambda_{max}$ (MeOH) nm (log$\varepsilon$): 346 (4.03), 260 (4.55), 219 (4.45); $^1$H-NMR (600 MHz, DMSO-$d_6$, 35°C) $\delta$: 12.63 (1H, s, 5-OH), 8.10 (2H, dd, $J$=8.1, 1.6 Hz, H-2′, 6′), 7.60 (3H, m, H-3′, 4′, 5′), 7.04 (1H, s, H-3), 6.86 (1H, d, $J$=2.2 Hz, H-6), 6.46 (1H, d, $J$=2.2 Hz, H-8), 5.35 (1H, d, $J$=1.5 Hz, H-1‴), 5.18 (1H, d, $J$=7.1 Hz, H-1″), 3.91 (1H, d, $J$=9.3 Hz, H-4‴a), 3.78 (1H, d, $J$=1.5 Hz, H-2‴), 3.74 (1H, brd, $J$=11.8 Hz, H-6″a), 3.66 (1H, d, $J$=9.3 Hz, H-4‴b), 3.56 (1H, dd, $J$=8.9, 7.0 Hz, H-2″), 3.53 (1H, m, H-5″), 3.50 (1H, br t, $J$=9.0 Hz, H-3″), 3.50 (1H, brd, $J$=11.8 Hz, H-6″b), 3.36 (1H, d, $J$=11.3 Hz, H-5‴a), 3.34 (1H, d, $J$=11.3 Hz, H-5‴b), 3.25 (1H, dd, $J$=8.9, 8.2 Hz, H-4″); $^{13}$C-NMR (150 MHz, DMSO-$d_6$, 35°C): Table 2; HR-ESI-MS (positive-ion mode) $m/z$: 571.1420 $[M+Na]^+$ (Calcd for $C_{26}H_{28}O_{13}Na$: 571.1422).

**Acid Hydrolysis of Schoepfiajasmin A (1) to Schoepfin B (16)** Schoepfiajasmin A (**1**) (9.2 mg) was hydrolyzed with 1 mL of 5% $H_2SO_4$ at 80°C for 1 h and then the reaction mixture was neutralized by the addition of Amberlite IRA96SB. The aqueous layer was partitioned with an equal amount of 1-BuOH and then evaporation of the 1-BuOH layer left 6.3 mg of schoepfin B (**16**).

Schoepfin B (**16**): Amorphous powder, $[\alpha]_D^{25}$ +20.2 ($c$=0.63, MeOH); $^1$H- and $^{13}$C-NMR: essentially the same as those reported for schoepfin B (**16**)[11]; HR-ESI-MS (positive-ion mode) $m/z$: 427.1362 $[M+Na]^+$ (Calcd for $C_{21}H_{24}O_8Na$: 427.1363).

**Sugar Analysis** About 500 $\mu$g of each compound, **1**–**4**, **7** and **8**, was hydrolyzed with 1 M HCl (0.1 mL) at 90°C for 2 h. The reaction mixtures were partitioned with an equal amount of EtOAc (0.1 mL), and the water layers were analyzed with a chiral detector (JASCO OR-2090*plus*) on an amino column [Asahipak $NH_2$P-50 4E, $CH_3CN$–$H_2O$ (4 : 1), 1 mL/min]. The

hydrolyzates of **1**–**3** each gave a peak for D-apiose at 6.1 min, that of **4** a peak for D-glucose at 19.4 min, and those of **7** and **8** peaks for D-apiose at 6.1 min and D-glucose at 19.4 min, with positive optical rotation signs. The peaks were identified by co-chromatography with authentic samples.

**Acknowledgments** The authors are grateful for access to the superconducting NMR instrument (JEOL JNM $\alpha$-400) at the Analytical Center of Molecular Medicine of the Hiroshima University Faculty of Medicine, and the LTQ Orbitrap XL HR-ESI-MS and the superconducting NMR instrument (JEOL ECA-600) at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University. This work was supported in part by Grants-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology of Japan (Nos. 22590006 and 23590130), the Japan Society for the Promotion of Science, and the Ministry of Health, Labour and Welfare. Thanks are also due to the Research Foundation for Pharmaceutical Sciences and the Takeda Science Foundation for the financial support.

## References

1) Tsuboi Y., Doi T., Matsunami K., Otsuka H., Shinzato T., Takeda Y., *J. Nat. Med.*, **65**, 617–622 (2010).
2) Tang W., Hioki H., Harada K., Kubo M., Fukuyama Y., *J. Nat. Prod.*, **71**, 1760–1763 (2008).
3) Buskas T., Söderberg E., Konradsson P., Fraser-Reid B., *J. Org. Chem.*, **65**, 958–963 (2000).
4) Miyaichi Y., Tomimori T., *Nat. Med.*, **49**, 350–353 (1995).
5) Okamura N., Yagi A., Nishioka I., *Chem. Pharm. Bull.*, **29**, 3507–3514 (1981).
6) Ono M., Ito Y., Ishikawa T., Kitajima J., Tanaka Y., Niiho Y., Nohara T., *Chem. Pharm. Bull.*, **44**, 337–342 (1996).
7) Kanho H., Yaoya S., Kawahara N., Nakane T., Takase Y., Masuda K., Kuroyanagi M., *Chem. Pharm. Bull.*, **53**, 361–365 (2005).
8) Sakai S., Kawaguchi K., Kamakura H., Kawahara N., Goda Y., *Jpn. J. Food Chem.*, **14**, 56–62 (2007).
9) Yoshizawa F., Deyama T., Takizawa N., Usmanghani K., Ahmad M., *Chem. Pharm. Bull.*, **38**, 1927–1930 (1990).
10) Shahat A. A., Abdel-Azim N. S., Pieters L., Vlietinck A. J., *Fitoterapia*, **75**, 771–773 (2004).
11) Huang C. F., Gan X. W., Bai H. Y., Ma L., Hu L. H., *Nat. Prod. Res.*, **22**, 623–627 (2008).
12) Ohashi H., Goto M., Imamura H., *Phytochemistry*, **16**, 1106–1107 (1977).
13) Hammami S., Jannet H. B., Bergaoui A., Ciavatta L., Cimino G., Mighri Z., *Molecule*, **9**, 602–608 (2004).
14) Ersöz T., Harput Ü. S., Saracoğlu I., Çaliş I., Ogihara Y., *Turk. J. Chem.*, **26**, 581–588 (2002).
15) El Antri A., Messouri I., Tlemçani R. C., Bouktaib M., El Alami R., El Bali B., Lachkar M., *Molecules*, **9**, 568–573 (2004).
16) Mustafa K. A., Kjaergaard H. G., Perry N. B., Weavers R. T., *Tetrahedron*, **59**, 6113–6120 (2003).
17) Slade D., Ferreira D., Marais J. P. J., *Phytochemistry*, **66**, 2177–2215 (2005).
18) Gaffield W., *Tetrahedron*, **26**, 4093–4108 (1970).
19) Werner S. R., Chen H., Jiang H., Morgan J. A., *Enzymatic*, **66**, 257–263 (2010).