173. Four Novel Glycosides from the Aphid *Pseudoregma bambusicola* T.

by **Guo-lin Zhang**[1])*, **Mei-yu He**, and **Qi-yi Xing**

The Chemistry Department of Peking University, Beijing 100871, The People's Republic of China

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Four novel glycosides, bambusicolasides III–VI (**1**–**4**), were isolated from the aphid *Pseudoregma bambusicola* T. The structures of **1**–**4** were elucidated by spectral evidence including FAB-MS and C,H-COSY, HMBC, and NOE difference experiments, and by hydrolysis. *In vitro* tests with these compounds showed little cytotoxic activity against human KB cells (< 10%).

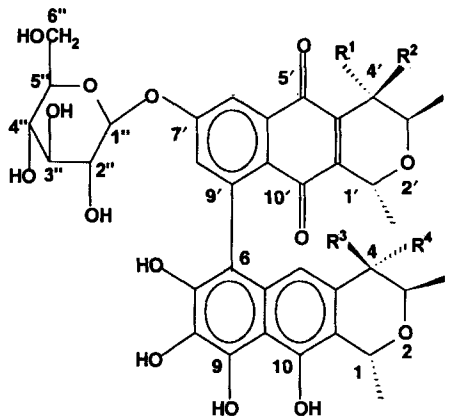
1. Introduction. – In a program searching for bioactive substances from organisms, our effort has been focused on the insects used in the Chinese folk medicine. Two new glycosides, bambusicolasides I and II having a 1*H*-naphtho[2,3-*c*]pyran aglycon moiety, have been isolated previously by chromatography of an extract from the aphid *Pseudoregma bambusicola* T. [1]. *P. bambusicola* T. is used directly or in the form of an EtOH extract in the Chinese folk medicine for the treatment of coughs and topically employed against hemiplegia [2]. In continuation of this work, we now isolated from the same aphid four new glycosides, bambusicolasides III–IV (**1**–**4**), containing the aglycon moiety 1*H*-naphtho[2,3-*c*]pyran or the quinoid 6,9′-bi[1*H*-naphtho[2,3-*c*]pyran]. Their structures were determined by FAB-MS, C,H-COSY and HMBC experiments, IR spectra, and hydrolysis. Because of their novel structures, the glycosides **1**–**4** were subjected to activity tests. *In vitro*, **1**–**4** showed little inhibitory effect (< 10%) against human KB cell lines at different concentrations.

Compounds **1**, **2**, and **4** are aphid C_{30} pigments which resemble protoaphin obtained from the aphid *Aphis fabae* [3] and other aphids [4]. This class of compounds may arise by coupling of 'monomeric-type' C_{15} pigments [5].

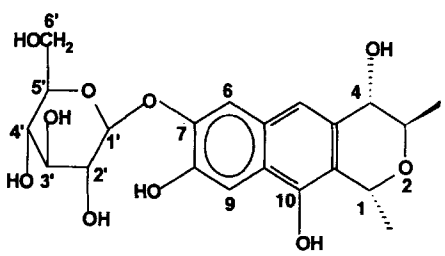
2. Results and Discussion. – Bambusicolaside III (**1**) was isolated as brown powder. Its fast-atom bombardment (FAB) MS (positive mode; *m/z* 712 ($[M + 2]^+$)) in its high-resolution FAB-MS (negative mode; *m/z* 710.2123) suggested the molecular formula $C_{36}H_{38}O_{15}$, which is in accordance with the thirty-six signals in its ^{13}C-NMR spectrum (*Table*), considering the reduction process normally associated with FAB-MS of quinones [6] [7].

The structure of **1** was elucidated by spectroscopic means and hydrolysis in 15% aqueous HCl solution which yielded D-glucose. The β-D-glucopyranosyl moiety of **1** gives rise, to a ^{1}H-NMR signal at δ 5.15 (*d*, *J* = 8 Hz, H–C(1″), and the fragment *m/z* 548 ($[M - Glc]^+$) in the FAB-MS. Four Me groups appearing at δ 21.60, 20.51, 19.98, and 17.76 in the ^{13}C-NMR are connected to tertiary C-atoms according to the multiplicity of their

[1]) Present address: Chengdu Institute of Biology, the Chinese Academy of Sciences, P.O. 416, Chengdu 610041.



1 $R^1=R^2=R^3=H$, $R^4=OH$
2 $R^1=R^4=OH$, $R^2=R^3=H$
4 $R^1=R^4=H$, $R^2=R^3=OH$



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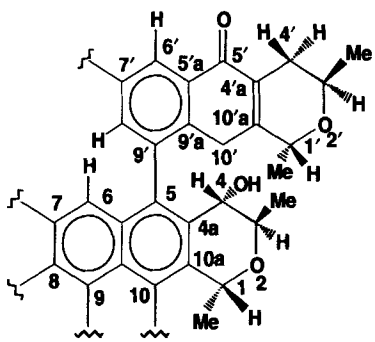

A

The configurations at C(1), C(1'), C(3), C(3'), C(4), and C(4') are only relative

^{1}H-NMR signals at δ 1.68 (*d*, J = 6 Hz), 1.51 (*d*, J = 6 Hz), 1.17 (*d*, J = 6 Hz), and 1.07 (*d*, J = 6.5 Hz). There is no NOE between the two pairs of the four Me groups. The presence of two C=O groups is established by the ^{13}C-NMR signals at δ 184.74 and 188.44 and the IR absorption at 1646 cm^{-1}. Besides the signals for the β-D-glucopyranosyl moiety, there are another five oxygenated aliphatic C-atoms at δ 63.93, 68.00 (two C-atoms), 70.43, and 72.07, the corresponding protons resonating at δ 5.30–3.90. In the ^{1}H-NMR, two *d* at δ 6.93 and 6.17 (each J = 2 Hz, 1 H) and one *s* at δ 6.74 (1 H) for aromatic protons are observed. C,H-COLOC and HMBC reveal the following correlations: *Me*–C(1)/C(10a); *H*–C(1)/C(10a); *H*–C(4)/C(4a), C(5), C(10a); *H*–C(6)/C(5), C(7), C(8); *Me*–C(1')/C(10'a); *H*–C(1')/C(3'), C(4'a); *Me*–C(3')/C(3'), C(4'); *H*–C(4')/C(4'a), C(5'); *H*–C(6')/C(5'), C(7'), C(9'a); *H*–C(8')/C(9'a), C(5). Together with the already mentioned data, they allow the partial structure **A** to be drawn. The molecular formula and the ^{13}C-NMR data suggest the presence of four aromatic OH groups. Because of the correlation between C(7') and H–C(1'') in the HMBC experiment, the β-D-glucopyranosyl can be located at C(7'). The two C=O groups are typical for quinones in view of their chemical shifts and the IR absorption. Thus, the C=O signal at δ 188.44 arises from C(10') which is connected to C(9'a) and C(10'a), thus forming a naphtho[2,3-*c*]pyran quinone skeleton. The four aromatic OH groups can only be assigned to C(7), C(8), C(9), and C(10). The coupling constant between H–C(3) and H–C(4) (5 Hz) suggests *trans* orientation of H–C(3) and H–C(4).

Bambusicolaside IV (**2**), a brown powder, had almost the same UV absorptions as those of **1**. Thirty-five signals were observed in the ^{13}C-NMR spectrum (*Table*). The presence of the β-D-glucopyranosyl moiety was established by the detection of D-glucose after hydrolysis of **2** in 15% aqueous HCl solution, and the remainder of the structure was deduced from spectroscopic data.

Table. *^{13}C-NMR Data* (CD_3OD) *of Bambusicolasides III–VI* (**1–4**). For **1** and **4**, 100 MHz; for **2** and **3**, 125 MHz; δ in ppm rel. to $SiMe_4$(= 0 ppm).

	1	**2**	**3**	**4**		**1**	**2**	**3**	**4**
C(1′)	68.00	71.12	104.01	67.99	C(4″)	71.09	71.12	–	71.08
C(2′)	–	–	74.69	–	C(5″)	78.64[d])	78.68[d])	–	79.40[d])
C(3′)	63.93	68.04	78.03[c])	71.79	C(6″)	62.34	62.57	–	62.37
C(4′)	30.84	71.54	71.40	61.12					
C(4′a)	143.63	146.88	–	142.66	C(1)	68.00	68.39	68.82	68.25
C(5′)	184.74	185.86	78.46[c])	183.90	C(3)	72.02	74.84	67.80	68.05
C(5′a)	136.28	137.26	–	133.60	C(4)	70.43	70.31	69.78	70.33
C(6′)	104.56	104.85	62.29	104.60	C(4a)	134.06	133.14	136.97	133.50
C(7′)	156.78	156.11	–	156.79	C(5)	124.01	124.06	119.15	124.10
C(8′)	102.99	103.31	–	103.04	C(5a)	125.19	125.34	137.51	125.49
C(9′)	131.78	131.83	–	131.56	C(6)	108.53	108.85	105.56[a])	108.34
C(9′a)	110.63	111.56	–	111.47	C(7)	166.21[b])	166.54[b])	156.49[b])	166.73[b])
C(10′)	188.44	189.40	–	189.15	C(8)	165.61[b])	165.80[b])	155.86[b])	165.81[b])
C(10′a)	146.18	146.88	–	146.69	C(9)	155.84	156.91	104.56[a])	155.83
Me–C(1′)	20.51	21.44	–	18.50	C(9a)	111.59	110.95	111.16	110.87
Me–C(3′)	21.60	17.80	–	18.02	C(10)	149.70	149.78	149.75	149.58
C(1″)	104.09	104.44	–	104.23	C(10a)	119.61	119.95	118.78	119.83
C(2″)	74.86	74.43	–	74.85	*Me*–C(1)	119.98	20.21	18.48	20.23
C(3″)	78.09[d])	78.13[d])	–	78.64[d])	*Me*–C(3)	17.76	18.62	16.99	16.68

[a]) [b]) [c]) [d]) The assignments for each compound maybe interchanged.

The ^{1}H-NMR signal at δ 5.12 (*d*, J = 7 Hz) arises from H–C(1″) of the β-D-glucopyranosyl moiety of **2**. Four tertiary Me groups appear at δ 1.10 (*d*, J = 6 Hz), 1.50 (*d*, J = 6.5 Hz), 1.17 (*d*, J = 6 Hz), and 1.66 (*d*, J = 6.5 Hz). In the ^{13}C-NMR of **2**, the signals above 100 ppm resemble closely those of **1**, except for an overlapped signal at δ 146.88 for two C-atoms instead of the separate signals for C(4′a) and C(10′a) of **1** (see *Table*). The FAB-MS (positive mode; *m/z* 728 ($[M + 2]^+$) and the HR-FAB-MS (negative mode); *m/z* 726.2068 ($M - C_{36}H_{38}O_{16}^-$) suggest that **2** possesses one more O-atom than **1**. In fact, the ^{13}C-NMR of **2** reveals that **2** has one more oxygenated CH group but one CH_2 group less than **1**. The integration of the ^{1}H-NMR signals at δ 3.90–4.10 of **2** (*ca.* 4 H) and those of **1** (3 H) confirms this conclusion. According to the correlations of C(7′) (156.11 ppm) with H–C(8′) (6.27 ppm) and H–C(1″) (5.13 ppm) in the HMBC experiment, the β-D-glucopyranosyl can be located at C(7′). The cross-peaks, H–C(4′) at δ 4.05 with C(5′) (185.86 ppm) and *Me*–C(3′) (1.10 ppm) with C(4′) (71.54 ppm), suggest that **2** bears one OH group at C(4′). The relative configurations at C(1), C(3), C(4), C(1′), C(3′), and C(4′) can be assigned by the lack of NOE's between Me–C(1) and Me–C(3) and Me–C(1′) and Me–C(3′), respectively, and by the coupling constants between H–C(3) and H–C(4) (5 Hz) and H–C(3′) and H–C(4′) (8 Hz).

Bambusicolaside V (**3**), is a white powder and has the composition $C_{21}H_{26}O_{10}$, as determined by FAB-MS (positive mode; *m/z* 439 ($[M + 1]^+$)) and HR-FAB-MS (negative mode; *m/z* 437.1506 ($[M - 1]^-$, $C_{21}H_{25}O_{10}^-$)). Again, D-glucose was formed on hydrolysis of **3** in 15% aqueous HCl solution, and the structure was corroborated by spectroscopic data.

The β-D-glucopyranosyl moiety of **3** gives rise to the ^{1}H-NMR signal at δ 5.08 (*d*, J = 8 Hz, H–C(1′)) and ^{13}C-NMR signal at δ 104.01 (C(1′)). The UV absorptions at λ_{max} 233, 281, 293, 306, 338, and 349 are typical for naphthalene derivatives. From ^{1}H-NMR and NOE's between H–C(3) and H–C(4), the two moieties CH(Me)–O (at δ 5.11 (*q*, J = 6.6 Hz, H–C(1)) and 1.47 (*d*, J = 6.6 Hz, Me–C(1))) and CH(OH)CH(Me)–O (at δ 4.23 (*s*, H–C(4)), 4.07 (*q*, J = 6 Hz, H–C(3)), and 1.29 (*d*, J = 6 Hz, Me–C(3)) can be postulated. Three *s* for aromatic protons resonate at δ 6.77 (*s*, H–C(5)), 6.96 (*s*, H–C(6)), and 7.09 (*s*, H–C(9)). Considering C(5) as the mutual correlating partner of H–C(4) and H–C(6) in the HMBC experiment, C(4) must be connected to C(4a) and C(1)

to C(10a). Because of the two correlations H–C(1′) and H–C(6) with C(7), the β-D-glucopyranosyl is located C(7). The significant NOE (5%) between H–C(6) and H–C(1′) supports this conclusion. Of the three OH groups suggested by the HR-FAB-MS and NMR data, two can be located at C(8) and C(10) from the observation of the correlations between H–C(1) and C(10) at δ 149.75, and H–C(9) and C(7) in the HMBC experiment. In the ^{1}H-NMR the *s* for H–C(4) reveals the relative configuration at C(3) and C(4). No enhancement of the Me–C(3) signal is observed when Me–C(1) is irradiated indicating that the two Me groups are *trans* oriented.

Bambusicolaside VI (**4**) was isolated as brown needles and showed almost the same UV absorptions and identical FAB-MS than **2**. Hydrolysis of **4** in 15% aqueous HCl solution yielded D-glucose, and the structure of **4** was established by spectroscopic means.

The β-D-glucopyranosyl moiety in **4** shows NMR signals at δ 5.15 (*d*, J = 8 Hz, H–C(1″)) and 104.23 (C(1″)). Thirty-six signals are observed in the ^{13}C-NMR (DEPT) spectrum of which the four at δ 16.68, 18.02, 18.50, and 20.23 are derived from tertiary Me groups, in view of the corresponding four *d*'s at δ 1.09 (*d*, J = 6 Hz), 1.50 (*d*, J = 6 Hz), 1.20 (*d*, J = 6 Hz), and 1.67 (*d*, J = 6 Hz). The main differences in the ^{13}C-NMR spectra of **2** and **4** are the signals of the aliphatic methine groups, *i.e.*, of C(1), C(3), C(4), C(1′), C(3′), and C(4′) (**2**: 68.39, 74.84, 70.31, 71.12, 68.04, and 71.54, respectively; **4**: δ 68.25, 68.05, 70.33, 67.99, 71.79, and 61.12, resp.). The C,H-COSY and HMBC experiments with **4** suggest the same structure as that of **2**. Thus, **4** is a stereoisomer of **2**. The relative configuration in **4** can be deduced from the coupling constants between H–C(3′) and H–C(4′) (2 Hz) and between H–C(3) and H–C(4) (negligible), as well as from the NOE difference experiments, in which no signal enhancement for any of the Me groups is observed when any one of the Me groups is irradiated. The 7′-position of the β-D-glucopyranosyl group is provided by the cross-peaks between H–C(1″) and C(7′) at δ 156.79, between H–C(6′) and C(7′), as well as between H–C(8′) and C(7′).

Experimental Part

General. Column chromatography CC: silica gel, 160–200 mesh. Optical rotation: *Perkin-Elmer-241* polarimeter; at 20°. UV Spectra: *Shimada-UV-240-UV/VIS* spectrophotometer; λ_{max}(log ε) in nm. CD's *JASCO spectropolarimeter*; λ([Θ]) in nm. IR Spectra: *SVX-200FT* spectrometer; KBr discs; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-AM-400* and *AMX-500* spectrometer, in CD_3OD using $SiMe_4$ as internal standard; δ in ppm, J in Hz; ^{13}C multiplicities from DEPT experiments. HR-FAB-MS (neg. mode) and FAB-MS (pos. mode): *Finnigan-MAT-90* and *ZAB-MS* spectrometer.

Animal Material. Samples of *P. bambusicola* T. were collected in 1995 in Sichuan Province, P.R. China, and authenticated in the Biology Department of Sichuan University, where a voucher specimen is deposited.

Extraction and Isolation. Dried *P. bambusicola* T. (4 kg) was soaked three times with 95% EtOH/H_2O (3 × 10 l). Evaporation of EtOH yielded 600 g of extract. The extract was then subjected to CC ($CHCl_3$/95% EtOH 5:1) to give six fractions *Fr. 1–6*. From *Fr. 5*, **1** (30 mg) and **2** (20 mg) were isolated by CC ($CHCl_3$/MeOH/Me_2CO 5:1:1). *Fr. 6* was separated by CC ($CHCl_3$/MeOH/MeCN 5:1:1) to yield **3** (30 mg) and **4** (80 mg).

Cytotoxicity Assays. The cytotoxicity of the compounds against human KB-cell lines was determined by the MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2*H*-tetrazolium bromide) colorimetric assay [8]. The cell line was plated at 5700 cells/well in 96-well microtiter plates. Threefold serial dilutions (10 µl) of the tested compounds in DMSO were added to the cells. For comparison, another two cells, without KB cells and the tested compound, and with KB cells but no tested compound, were established. Then the plates were incubated at 37°, 5% CO_2, and saturated humidity for 96 h. MTT (10 µl, 5 mg/ml) was added to each well, and the plates were incubated under the same conditions as mentioned above for 4 h. Formazan crystals were redissolved in DMSO, and the *OD* values of each well were measured at 540 nm with ELISA (*DG-3022A*), thereupon the inhibitory ratio of each compounds against human KB-cell lines were calculated. The experiment was repeated. The results of the experiments showed that all four compounds with a concentration of 30 µg/ml had a inhibitory ratio against human KB-cell lines of < 10%, *i.e.*, the IC_{50} of **1**–**4** against KB cells was > 30 µg/ml. ADR was used as a standard (IC_{50} 0.03 µg/ml).

Bambusicolaside III (= *(1R*,1R*,3R*,4S*)-7′-[(β-D-Glucopyranosyl)oxy]-3,3′,4,4′-tetrahydro-4,7,8,9,10-pentahydroxy-1,1′,3,3′-tetramethyl-6,9′-bi[1H-naphtho[2,3-c]pyran]-5′,10′-dione*; **1**): Brown powder. M.p. > 215° (uncorr.). $[\alpha]_D$ = + 133.0 (*c* = 1.5, MeOH). UV: 224 (4.71), 230 (sh), 297 (4.14), 310 (sh), 342 (3.73), 356 (3.73), 450 (3.55). IR: 3436, 1646, 1614, 1588, 1440, 1384, 1364, 1296, 1257, 1181, 1071, 1074. CD (1.41 mM, EtOH): 266

(−41890, min), 297 (−19170, min), 345 (+3550, max), 430 (+4970, max). ^{1}H-NMR (400 MHz): 3.90 (*m*, H−C(2)); 2.31 (*dd*, ^2J = 18, J(4′α,3′α) = 3, H−C(4′α)); 1.88 (*dd*, ^2J = 18, J(4′β,3′α) = 10, H−C(4′β)); 6.93 (*d*, J(6′,8′) = 2, H−C(6′)); 6.17 (*d*, J(8′,6′) = 2, H−C(8′)); 4.88 (*m*, H−C(1′)); 1.17 (*d*, J(Me−C(3′), 3′) = 6, Me−C(3′)); 1.51 (*d*, J(1′, Me−C(1′)) = 6, Me−C(1′)); 4.04 (*qd*, J(3, Me−C(3)) = 6, J(3,4) = 5, H−C(3)); 3.95 (*d*, J(4,3) = 5, H−C(4)); 6.74 (*s*, H−C(5)); 5.22 (*q*, J(1, Me−C(1)) = 6, H−C(1)); 1.07 (*d*, J(3, Me−C(3)) = 6, Me−C(3)); 1.68 (*d* J(1, Me−C(1)) = 6, Me−C(1)). ^{13}C-NMR: *Table*. FAB-MS (pos.): 712 ([M + 2]$^+$), 548 ([M + 1 − Glc]$^+$), 531. HR-FAB-MS (neg.): 710.2131 (M^-, $C_{36}H_{38}O_{15}^-$, 100; calc. 710.2211), 562 (22), 547 (40), 340 (29), 325 (35), 310 (24).

Bambusicolaside IV (= *(1*R*,1′R*,3R*,3′R*,4S*,4′S*)-7′-[(β-*D*-Glucopyranosyl)oxy]-3,3′4,4′-tetrahydro-4,4′,7,8,9,10-hexahydroxy-1,1′,3,3′-tetramethyl-6,9′-bi[1H-naphtho[2,3-c]pyran]-5′,10′dione*; **2**): Brown powder. M.p. > 240° (uncorr.). [α$_D$] = + 144.0 (*c* = 1.3, MeOH). UV: 232 (4.67), 298 (4.10), 344 (3.73), 356 (3.53), 456 (3.45). IR: 3473, 3402, 3377, 1642, 1621, 1452, 1368, 1274, 1168, 1074. CD (1.38 mM, EtOH): 265 (−25410, max), 305 (−11616, min), 350 (+5445, max), 450 (+8712, max). ^{1}H-NMR (500 MHz): 4.00 (*m*, H−C(3′)); 4.05 (*d*, J(4′,3′) = 8, H−C(4′)); 6.96 (*d*, J(6′,8′) = 2, H−C(6′)); 6.27 (*d*, J(8′,6′) = 2, H−C(8′)); 4.73 (*q*, J(1′, Me−C(1′)) = 6.5, H−C(1′)); 1.10 (*d*, J(Me−C(3′),3′) = 6, Me−C(3′)); 1.50 (*d*, J(Me−C(1′),1′) = 6.5, Me−C(1′)); 512 (*d*, J(1″,2″) = 7, H−C(1″)); 3.77, 4.00 (2*m*, 1 H−C(6″)); 3.61 (*m*, H−C(3)); 3.90 (*d*, J(4,3) = 5, H−C(4)); 6.71 (*s*, H−C(6)); 5.16 (*q*, J(1,Me−C(1)) = 6.5, H−C(1)); 1.17 (*d*, J(Me−C(3),3) = 6, Me−C(3)); 1.66 (*d*, J(Me−C(1),1) = 6.5, Me−C(1)). ^{13}C-NMR: *Table*. FAB-MS (pos.) *m/z*: 728 ([M + 2]$^+$), 564, 547, 531. HR-FAB-MS (neg.) *m/z* (%): 726.2068 (M^-, $C_{36}H_{38}O_{16}$, calc.: 710.2159) (30), 711 (15), 437 (75), 325 (29), 290 (100), 259 (80), 231 (58).

Bambusicolaside V (= *(1*R*,3R*,4S*)-7-[(β-*D*-Glucopyranosyl)oxy]-3,4-dihydro-1,3-dimethyl-1H-naphtho-[2,3-c]pyran-4,8,10-triol*; **3**): White powder. M.p. > 186° (uncorr.). [α]$_D$ = + 91.0 (*c* = 7.0, MeOH). UV: 233 (4.60), 281 (3.72), 293 (3.72), 306 (3.73), 338 (3.53), 349 (3.56). IR: 3400, 1639, 1621, 1587, 1386, 1305, 1294, 1169, 1099, 1074, 1046, 1020. CD (2.28 mM, EtOH): (280 (+3161, max), 290 (+3924, max), 303 (+3379, max), 340 (+981, max). ^{1}H-NMR (500 MHz): 4.07 (*d*, J(3, Me−C(3)) = 6, H−C(3)); 4.23 (*s*, H−C(4)); 6.77 (*s*, H−C(5)); 6.96 (*s*, H−C(6)); 7.09 (*s*, H−C(9)); 5.11 (*q*, J(1,Me−C(1)) = 6.6, H−C(1)); 1.29 (*d*, J(Me−C(3),3) = 6, Me−C(3)); 1.47 (*d*, J(Me−C(1),1) = 6.6, Me−C(1)); 5.08 (*d*, J(1′,2′) = 8, H−C(1′)). ^{13}C-NMR: *Table*. FAB-MS (pos.): 439 ([M + 1]$^+$), 421, 276, 259. HR-FAB-MS (neg.): 437.1506 ([M − 1]$^-$, $C_{21}H_{25}O_{10}^-$; calc. 437.1448), 433.2789, 421.7428, 367.1816.

Bambusicolaside VI (= *(1*R*,1R*,3R*,3′R*,4R*,4′R*)-7′[(β-*D*-Glucopyranasyl)oxy]-3,3′,4,4′-tetrahydro-4,4′,7,8,9,10-hexahydroxy-1,1′,3,3′-tetramethyl-6,9′-bi[1H-naphtho[2,3-c]pyran]-5′,10′-dione*; **4**): Brown needles (MeOH). M.p. > 220° (uncorr.). [α]$_D$ = + 101.0 (*c* = 1.1, MeOH). UV: 226 (4.66), 298 (4.06), 305 (sh), 344 (3.67), 356 (3.68), 458 (3.58). CD (1.38 mM, EtOH): 265 (−36400, min), 300 (−37128, min), 353 (+8008, max), 435 (+13104, max). ^{1}H-NMR (400 MHz): 4.00 (*m*, H−C(3′)); 4.08 (*d*, J(4′,3′) = 2, H−C(4′)); 6.95 (*d*, J(6′,8′) = 2, H−C(6′)); 6.23 (*d*, J(8′,6′) = 2, H−C(8′)); 4.93 (*q*, J(1, Me−C(1)) = 6, H−C(1)); 1.09 (*d*, J(Me−C(3′),3′) = 6, Me−C(3′)); 1.50 (*d*, J(Me−C(1′),1′) = 6, Me−C(1′)); 5.15 (*d*, J(1″,2″) = 8, H−C(1″)); 3.91 (*m*, H−C(3)); 3.95 (*s*, H−C(4)); 6.74 (*s*, H−C(6)); 5.20 (*q*, J(1, Me−C(1)) = 6, H−C(1)); 1.20 (*d*, J(Me−C(3),3) = 6, Me−C(3)); 1.67 (*d*, J(Me−C(1),1) = 6, Me−C(1)). ^{13}C-NMR: *Table*. FAB-MS (pos.): 728, 711, 564, 547, 530, 515. FAB-MS (neg.): 726.2111 (M^-, $C_{36}H_{38}O_{16}^-$, 100; calc. 726.2159), 710 (20), 564 (27), 289 (32).

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