New Jujubogenin Glycosides from *Colubrina asiatica*

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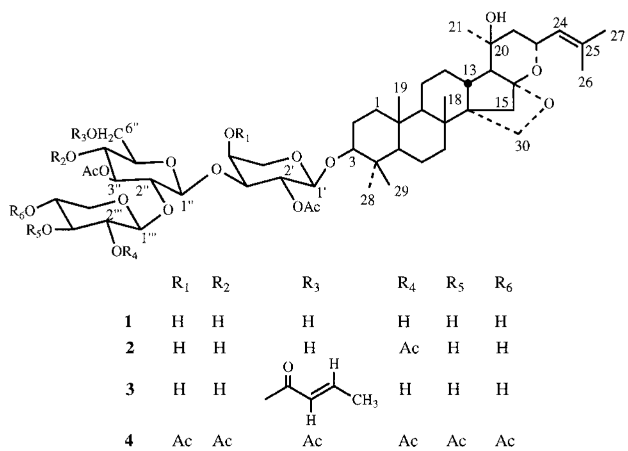
Three new jujubogenin glycosides, namely, 3″-*O*-acetylcolubrin (**1**); 3″,2‴-*O*-diacetylcolubrin (**2**), and 3″-*O*-acetyl-6″-*O*-*trans*-crotonylcolubrin (**3**), were isolated from the leaves of *Colubrina asiatica*, in addition to the known colubrin, rutin, and kaempferol 3-*O*-rutinoside. Compounds **1**−**3** were isolated and purified via a combination of chromatographic procedures, and determined structurally using spectroscopic methods.

A literature survey has indicated that *Colubrina asiatica* (L.) Brongn. (Rhamnaceae), a scandent glabrous shrub widely distributed in tropical Asia,[1] produces two jujubogenin glycosides, colubrin and colubrinoside, and several flavonoid glycosides in the leaves,[2] as well as the bisbenzylisoquinoline alkaloid *O*-methyldauricine in the bark.[3] We have reexamined the chemical constituents of the leaves of *C. asiatica* in the present investigation. A combination of several chromatographic techniques has led to the isolation of six glycosides, including four jujubogenin glycosides, **1**−**3** and colubrin, and two flavonoid glycosides, rutin[4] and kaempferol 3-*O*-rutinoside.[5] The structural characterization of **1**−**3** is described in the following paragraphs.



The triterpenoid glycosides of this plant contain ester functional groups and were found to be present mostly in the $CHCl_3$-soluble extract. Being quite polar, compounds **1**−**3** and colubrin were separated either using a RP_{18} column (**3** and colubrin) or by droplet counter-current chromatography (DCCC) (**1** and **2**). The NMR spectroscopic data of colubrin have previously been published in C_5D_5N.[2] To facilitate comparison with its analogues, the spectral data of colubrin, that is, 3-*O*-[*β*-D-xylopyranosyl (1→2)-*β*-D-glucopyranosyl (1→3)-α-L-2-*O*-acetyl-arabinopyranosyl] jujubogenin, measured in CD_3OD, were assigned by analysis of the 2D NMR spectra (COSY, TOCSY, HMQC, and HMBC), and are listed in the Supporting Information.

Compounds **1**−**3** were found to possess the same aglycon moiety, jujubogenin, as evidenced by the close similarity of the ^{13}C NMR data due to this aglycon moiety in comparison to colubrin. Acid hydrolysis of these three glycosides and colubrin yielded ebelin lactone, which also supported the presence of a common aglycon.[2,6] Of these compounds, the ^{1}H NMR spectra of colubrin and compounds **1** and **2** displayed one, two, and three acetyl methyl signals, respectively, and their peracetylation products were identical, indicating that these three compounds possess the same skeleton, including the sugar linkages, and differ only in the degree of acetylation.

Compound **1**, a white amorphous solid, had a molecular formula of $C_{50}H_{78}O_{19}$, as deduced from ^{13}C NMR (CPD and DEPT) data and FABMS, which showed a fragment ion at *m*/*z* 1005 corresponding to $[M + Na]^+$. It possesses two *O*-acetyl groups, as reflected by its ^{1}H and ^{13}C NMR spectra, one more than colubrin. Its IR spectrum also revealed an absorption (1739 cm^{-1}) for the presence of acetyl groups. Its ^{13}C NMR spectrum revealed three anomeric carbon signals at *δ* 105.8, 104.9, and 103.2. Comparison of its ^{13}C NMR data (C_5D_5N) with the reported data of colubrin[2] indicated almost identical chemical shifts for those carbons in the xylose unit, suggesting this sugar to be nonacetylated. Analysis of its COSY-45 and TOCSY spectra verified the coupling and chemical shift of each sugar proton. The key coupling signals included *δ* 4.59 (H-1′) ↔ 5.92 (H-2′) ↔ 4.12 (H-3′) ↔ 4.49 (H-4′), and *δ* 5.11 (H-1″) ↔ 4.08 (H-2″) ↔ 5.82 (H-3″) ↔ 4.25 (H-4″), *δ* 4.95 (H-1‴) ↔ 3.93 (H-2‴) ↔ 4.07 (H-3‴) in each sugar unit, suggesting the two *O*-acetylated groups were located at C-2 of the arabinose unit ($\delta_{H-2'}$ 5.92, dd, $J = 7.8$, 9.0 Hz) and C-3 of glucose unit ($\delta_{H-3''}$ 5.82, dd, $J = 9.1$, 9.1 Hz). The methyl proton signals in the aglycon portion (Table 1) were also designated by NOED experiments. The proton-bearing carbon signals (Table 1) were assigned directly from the analysis of the HMQC spectrum. Using the distinct methyl signals and acetylated carbinoyl proton signals as markers, the signals of quaternary carbons, including acetyl carbons, were assigned by analyzing the HMBC spectrum (Table 1). Thus, **1** was elucidated as 3″-*O*-acetylcolubrin.

Compound **2**, a white amorphous solid, had a molecular formula of $C_{52}H_{80}O_{20}$, as deduced from FABMS, which showed a fragment ion at *m*/*z* 1047 corresponding to $[M + Na]^+$, and its ^{13}C NMR (CPD and DEPT) data. It possesses three *O*-acetyl groups, as reflected by its ^{1}H and ^{13}C NMR spectra, one more than **1**. Its ^{1}H NMR spectrum was similar to that of **1** and revealed all three acetylated carbinoyl protons (*δ* 5.90, dd, $J = 10.0$, 7.9 Hz; *δ* 5.72, dd, $J = 9.3$, 9.1 Hz; and *δ* 5.51 dd, $J = 9.6$, 7.5 Hz) as possessing two diaxial couplings, suggesting their axial orientation. Analysis of its COSY-45 and TOCSY spectra verified the coupling and chemical shift of each sugar

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Table 1. ^{1}H and ^{13}C NMR Data (δ/ppm) and HMBC Data of **1** in C_5D_5N (400 MHz)

position	δ_H mult. (*J*/Hz)[a]	δ_C (mult.)[b]	HMBC (H→C)
1	0.72, 1.48	38.5 t	
2	1.74, 2.03	26.6 t	
3	3.11 dd (4.1,11.7)	88.8 d	4, 28, 29
4		39.4 s	
5	0.64 m	56.0 d	
6	1.25, 1.83	18.3 t	
7	1.37, 1.49	36.0 t	
8		37.5 s	
9	0.85	53.0 d	
10		37.2 s	
11	1.32, 1.53	21.8 t	
12	1.77, 1.92	28.5 t	17
13	2.79 m	37.1 d	17, 20, 30
14		53.8 s	
15	1.52	36.9 t	13, 16, 17
	2.47		14, 16
16		110.6 s	
17	1.36	54.0 d	12, 21
18	1.05 s	18.9 q	7, 8, 9, 14
19	0.66 s	16.2 q	1, 5, 9, 10
20		68.5 s	
21	1.36 s	30.1 q	17, 20, 22
22	1.63, 1.74	45.5 t	23
23	5.18 br dd (7.8,9.6)	68.6 d	24, 25
24	5.51 br d (7.8)	127.1 d	26, 27
25		134.2 s	
26	1.65 s	18.4 q	25, 27
27	1.69 s	25.6 q	25, 26
28	1.02 s	27.8 q	3, 4, 5, 29
29	0.84 s	16.5 q	3, 4, 5, 28
30	4.13, 4.24	65.8 t	13, 16
ara			
1′	4.59 d (7.8)	104.9 d	3, 3′
2′	5.92 dd (7.8, 9.0)	71.7 d	O*C*OMe-2′, 1′, 3′
3′	4.12 dd (2.8, 9.0)	81.2 d	1′, 2′, 1″
4′	4.49 br s	69.1 d	2′, 3′
5′	3.65 br d(11.4)	66.7 t	1′, 3′, 4′
	4.18		
O*C*OMe-2′		169.4 s	
OCO*Me*−2′	2.16 s	21.61 q	O*C*OMe-2′
glc			
1″	5.11 d (7.2)	103.2 d	3′, 2″, 5″
2″	4.08	79.0 d	1″, 3″, 1‴
3″	5.82 dd (9.1,9.1)	78.6 d	O*C*OMe-3″, 2″, 4″
4″	4.25	69.3 d	3″, 6″
5″	3.98 br dd (3.6, 9.3)	78.1 d	
6″	4.29, dd (3.6, 12.2)	62.0 t	
	4.42		
O*C*OMe-3″		171.0 s	
OCO*Me*−3″	2.13 s	21.56 q	O*C*OMe-3″
xyl			
1‴	4.95 d (8.0)	105.8 d	2″, 5‴
2‴	3.93 dd (8.0, 8.2)	74.6 d	1‴, 3‴
3‴	4.07	78.6 d	2‴
4‴	4.25	71.2 d	3‴, 5‴
5‴	3.63 dd (9.4, 11.1)	67.3 t	1‴, 3‴, 4‴
	4.42 br d (11.1)		

[a] Data without multiplicities were obtained using the COSY-45 and HMQC pulse sequences. [b] Multiplicities were obtained from DEPT experiments.

proton. The key coupling signals included δ 4.59 (H-1′) ↔ 5.90 (H-2′) ↔ 4.04 (H-3′), δ 5.04 (H-1″) ↔ 3.99 (H-2″) ↔ 5.72 (H-3″) ↔ 4.20 (H-4″) and δ 5.02 (H-1‴) ↔ 5.51 (H-2‴) ↔ 4.11 (H-3‴) in each sugar unit, suggesting that the three *O*-acetylated groups were located at C-2 of the arabinose unit ($\delta_{H-2'}$ 5.90), C-3 of the glucose unit ($\delta_{H-3''}$ 5.72), and C-2 of the xylose unit ($\delta_{H-2'''}$ 5.51). The HMBC data (Table 2) revealed the sugar linkages in **2** to be the same as those in colubrin[2] and supported the location of three acetoxyl groups as indicated above. Therefore, compound **2** was assigned as 3″,2‴-*O*-diacetylcolubrin.

Compound **3**, a white amorphous solid, had a molecular formula of $C_{54}H_{82}O_{20}$, as deduced from FABMS, which showed a fragment ion at *m/z* 1073 corresponding to $[M + Na]^+$, and its ^{13}C NMR (CPD and DEPT) data. Its ^{1}H NMR spectrum displayed signals for two *O*-acetyl groups at δ 2.17 (3H, s), 2.31 (3H, s), and one *O*-*trans*-crotonyl group at δ 5.93 (1H, dq, *J* = 14.4, 1.3 Hz, α-H), 7.00 (1H, dq, *J* = 14.4, 6.8 Hz, β-H), and 1.60 (3H, dd, *J* = 6.8, 1.3 Hz, γ-H). The presence of a crotonyl moiety was supported by a UV absorption maximum at λ 206 nm (H_2O). A COSY-45 spectrum of **3** verified the coupling and chemical shift of each sugar proton. The key coupling signals included δ 4.63 (H-1′) ↔ 5.90 (H-2′), δ 4.98 (H-1″) ↔ 4.06 (H-2″) ↔ 5.92 (H-3″) ↔ 4.93 (H-4″) ↔ 4.09 (H-5″) ↔ 4.86 (H-6″a) ↔ 5.19 (H-6″b) and δ 4.93 (H-1‴) ↔ 3.91 (H-2‴) in each sugar unit. These data and coupling patterns of each proton (Table 2) suggested that **3** contains a sugar moiety identical to that in **1** and an additional crotonyl substituent at C-6 of glucose. This proposal was supported by comparison of its ^{13}C NMR spectrum with that of **1**, revealing very similar chemical shifts in the arabinose and xylose units, with the C-6 signal of glucose in **3** being shifted downfield (δ 61.5 in **1**, δ 64.2 in **3**). The HMBC spectrum (Table 2) of **3** displayed the coupling of H-1′ (δ 4.63, ara) to C-3 (δ 88.9), H-1″ (δ 4.98, glc) to C-3′ (δ 81.8, ara), H-1‴ (δ 4.93, xyl) to C-2″ (δ 78.3, glc), confirming the linkage of these three monosaccharides as depicted for **1** and **2**. Thus, **3** possesses a 3-*O*-[3-*O*-(2-*O*-β-D-xylopyranosyl-β-D-glucopyranosyl)-α-L-arabinopyranosyl] moiety. The HMBC spectrum also revealed the correlations of H-1′ (δ 4.63, ara) to C-3 (δ 88.9); H-2′ (δ 5.90) to 2′-O*C*OMe (δ 169.6); H-3″ (δ 5.92) to 3″-O*C*OMe (δ 171.9); and H-6″ (δ 4.86 and 5.19, glc) to C-1 of the crotonyl group (δ 166.4). These coupling data confirmed the acylated positions in the sugar moieties as indicated above. The above information enabled **3** to be assigned as 3″-*O*-acetyl-6″-*O*-*trans*-crotonylcolubrin.

Experimental Section

General Experimental Procedures. Optical rotations were determined with a JASCO DIP-370 digital polarimeter. UV spectra were recorded on a Hitachi 2000 UV spectrophotometer (MeOH). IR spectra were recorded on a Perkin-Elmer 1760-X Infrared FT spectrometer (KBr). ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AMX-400 NMR spectrometer (CD_3OD, δ_H 3.30, δ_C 49.0; C_5D_5N, δ_H 8.71, δ_C 149.9; $CDCl_3$, δ_H 7.24) using Bruker's standard pulse programs: in the HMQC and HMBC experiments, Δ = 1 s and *J* = 140, 8 Hz, respectively, the correlation maps consisted of 512 × 1K data points per spectrum, each composed of 16 to 64 transients. FABMS were recorded using a JEOL JMX-HX110 mass spectrometer (matrix, 4-nitrobenzyl alcohol). Partition chromatography was performed on Sanki centrifugal partition chromatography (CPC) instruments (LLI-7 type: 6 L; LLN type: 6 1000E cartridges, 410 mL) and DCC-300S (Tokyo Rikakikai Co. Ltd). Si gel TLC analysis was performed using the lower layer of the solvent system, $CHCl_3$−*i*-PrOH−MeOH−H_2O (5:1:6:4), as the developing system.

Plant Material. The leaves of *Colubrina asiatica* (L.) Brongn. for this study were collected in June 1996, from Dong-Sar Island, Kaohsiung County, Taiwan. A voucher specimen (no. NTUPH-19960601) has been deposited in the School of Pharmacy, National Taiwan University.

Extraction and Isolation. The ground dried leaves (6.5 kg) were percolated with 95% EtOH (31 L × 6). The EtOH extract (1.10 kg) was partitioned between H_2O (1.5 L) and $CHCl_3$ (1 L × 3). The $CHCl_3$-soluble fraction (580 g) was triturated with hexane (0.5 L × 3) to give fractions soluble in hexane (100 g) and $CHCl_3$ (459 g). The H_2O layer was partitioned against *n*-BuOH (1 L × 3) to give a fraction soluble

Table 2. ^{1}H and ^{13}C NMR Data (δ/Ppm) and HMBC Data of the Glycone Moieties of **2** and **3** in C_5D_5N (400 MHz)[a]

position	**2**			**3**[d]		
	δ_H m[b] (J/Hz)	δ_C m[c]	HMBC (H→C)	δ_H m[b] (J/Hz)	δ_C m[c]	HMBC (H→C)
Ara						
1′	4.59 d (7.9)	104.9 d	3	4.63 d (7.8)	104.9 d	3
2′	5.90 dd (10.0, 7.9)	71.5 d	O*C*OMe-2′, 1′, 3′	5.90 dd (10.4, 7.8)	71.4 d	O*C*OMe-2′, 1′, 3′
3′	4.04 dd (10.0, 3.2)	81.3d	1′, 2′, 1″	4.04 m	81.8 d	1′, 2′, 1″
4′	4.44 br m	69.0 d	2′, 3′	4.45 m	69.3 d	
5′	3.63, 4.14	66.7 t	1′, 3′, 4′	3.73	66.8 t	1′
				4.20		1′, 3′, 4′
O*C*OMe-2′		169.5 s			169.6 s	
OCO*Me*-2′	2.29 s	21.7 q	O*C*OMe-2′	2.17 s	21.6 q	O*C*OMe-2′
glc						
1″	5.04 d (7.0)	102.9 d	3′	4.98 d (7.6)	103.3 d	3′, 3″, 5″
2″	3.99 dd (9.1, 7.0)	77.9 d	1″, 1‴	4.06 dd (9.0, 7.6)	78.3 d	3″, 4″
3″	5.72 dd (9.3, 9.1)	78.7 d	2″, 4″, O*C*OMe-3″	5.92 dd (9.3, 9.0)	75.9 d	O*C*OMe-3″, 2″, 4″
4″	4.20 m	69.2 d	2″, 3″	4.93 dd (9.5, 9.3)	74.5 d	6″
5″	3.93 m	77.9 d	3″	4.09 m	74.0 d	1″
6″	4.30, 4.39	61.9 t	4″	4.86 dd (11.3, 7.7)	64.2 t	5″, O*C*O-6″
				5.19 br d (11.3)		
O*C*OMe-3″		170.6 s	O*C*OMe-3″		171.9 s	
OCO*Me*−3″	2.10 s	21.2 q	OCO*Me*−3″	2.31 s	21.9 q	O*C*OMe-3″
xyl						
1‴	5.02 d (7.5)	102.6 d	2″, 5‴	4.93 d (7.7)	105.6 d	2″
2‴	5.51 dd (9.6, 7.5)	75.0 d	1‴, 3‴, O*C*OMe-2‴	3.91 dd (8.6, 7.7)	74.6 d	1‴, 3‴
3‴	4.11 m	76.6 d	2‴, 4‴	4.06 m	78.5 d	1‴, 4‴
4‴	4.32 m	71.4 d	3‴, 5‴	4.23 m	71.1 d	3‴
5‴	3.65, 4.42	67.4 t	1‴, 3‴, 4‴	3.65 dd (11.1, 10.2)	67.2 t	1‴, 3‴, 4‴
				4.42 dd (11.1, 5.3)		1‴, 3‴
O*C*OMe-2‴		170.4 s				
OCO*Me*−2‴	2.23 s	21.2 q	O*C*OMe-2‴			

[a] ^{1}H and ^{13}C NMR data of **2** and **3** in the aglycon moiety were almost identical to those of **1** and thus are not listed here. [b] Data without multiplicities were obtained using the COSY-45, TOCSY, and HMQC pulse sequences. [c] Multiplicities were obtained from DEPT experiments. [d] Chemical shifts of 6″-*O*-*trans*-crotonyl group in **3**: δ_C 166.4 (s), 123.1 (d, C_α), 145.1 (d,C_β), 17.8 (q, C_γ); δ_H 5.93 (dq, J = 14.4, 1.3, H_α), 7.00 (dq, J = 14.4, 6.8, H_β), 1.60 (dd, J = 6.8, 1.3, H_γ). HMBC: H_α to C_γ, H_β to C_1, C_α and C_γ, H_γ to C_α and C_β.

in *n*-BuOH (110 g). Part of the $CHCl_3$-soluble fraction (100 g of 459 g) was fractionated on a Sanki LLI-7 type CPC using the aqueous layer and organic layer of the solvent system $CHCl_3-MeOH-H_2O$ (2:2:1) as mobile and stationary phase, respectively. The eluents were pooled in five fractions, as a result of Si gel TLC visualized by anisaldehyde spray reagent. Fraction 1 (8 g) was separated on two successive Sephadex LH-20 columns, eluted with MeOH and $MeOH-H_2O$ (1:1), respectively, and a Lobar RP_{18} (size A) to give rutin[4] (50 mg) and kaempferol 3-*O*-rutinoside[5] (50 mg). Part of fraction 2 (8 g of 26 g) was fractionated on a Sephadex LH-20 column, eluted with $CHCl_3-MeOH$ (1:2), to give three subfractions. Subfraction 2 (180 mg) was separated on a Lobar RP_{18} column eluted by $MeOH-H_2O$ (3:2) to give **3** (51 mg). A portion of fraction 3 (0.9 g of 7.0 g) from the first CPC fractionation was separated on a flash Si gel column (230−400 mesh) eluted by the lower layer of the solvent system $CHCl_3-MeOH-H_2O$ (13:7:4) and subsequent Lobar RP_{18} column [($MeOH-H_2O$ (7:3)] to give colubrin[2] (30 mg). Fraction 4 (2.4 g), obtained from the first CPC fractionation, was further fractionated using CPC and DCCC, both using the same delivery system as the first CPC, and finally separated on a flash Si gel column (230−400 mesh) eluted by the lower layer of the solvent system $CHCl_3-EtOH-H_2O$ (17:7:4) to give **2** (18 mg) and **1** (10 mg).

3″-*O*-Acetylcolubrin (1): amorphous solid, R_f 0.31; $[\alpha]^{24}_D$ −7.4° (*c* 0.6, MeOH); IR ν_{max} 3424, 2948, 1740, 1642, 1450, 1373, 1254 cm^{-1}; ^{1}H and ^{13}C NMR, see Tables 1 and 2; FABMS (positive) *m/z* $[M + K]^+$ 1021 (6), $[M + Na + 1]^+$ 1006 (55), $[M + Na]^+$ 1005 (100), $[M - H_2O+Na]^+$ 987 (6), $[M - H_2O]^+$ 964 (8), $[M - xyl - glc(OAc) + H + K]^+$ 685 (39), $[M - aglycon(OH) + K]^+$ 549 (3).

3″,2‴-*O*-Diacetylcolubrin (2): amorphous solid, R_f 0.52; $[\alpha]^{24}_D$ −12.5° (*c* 0.16, MeOH); IR ν_{max} 3420 (br s), 2950, 1739, 1640, 1452, 1370, 1250, 1050, 818 cm^{-1}; ^{1}H and ^{13}C NMR, see Tables 1 and 2; FABMS (positive) *m/z* $[M + Na]^+$ 1047 (100), $[M - Ac + Na + H]^+$ 1005 (17), $[M - HOAc + Na]^+$ 987 (8), $[M - HOAc + H]^+$ 965 (5), $[M - xyl(OAc) - glc(OAc) + H + Na]^+$ 669 (5), $[glycone(OH) - H_2O + H + K]^+$ 593 (12), $[aglycon(OH) - H_2O + Na]^+$ 477 (10).

3″-*O*-Acetyl-6″-*O*-*trans*-crotonylcolubrin (3): amorphous powder, R_f 0.28; $[\alpha]^{24}_D$ +2.0° (*c* 0.5, MeOH); UV (H_2O) λ_{max} (log ε) 206 (4.64) nm; IR ν_{max} 3440 (br s), 2948, 1740, 1650, 1450, 1374, 1240, 1040, 805 cm^{-1}; ^{1}H and ^{13}C NMR, see Tables 1 and 2; FABMS (positive) *m/z* $[M + K]^+$ 1089 (55), $[M + Na]^+$ 1073 (100), $[M - xyl - OAc + H]^+$ 859 (10), $[aglycon(OH) - 2H_2O + H]^+$ 437 (84).

Acid Hydrolysis of 1−3 and Colubrin. Part of the $CHCl_3$-soluble fraction (23 g) was chromatographed over a Sephadex LH-20 column eluted with MeOH to give two fractions. Part of the fraction (0.5 g of 13.7 g), containing jujubogenin glycosides was dissolved in 36% $HCl-EtOH-H_2O$ (1:2:2, 10 mL) and placed in a 50-mL flask. The solution was stirred for 2.5 h under reflux. The solution after evaporation of organic solvent was neutralized with powder K_2CO_3 and diluted with H_2O (50 mL), partitioned with $CHCl_3$ (50 mL × 3). The $CHCl_3$ layer was dried over Na_2SO_4 and evaporated to give a residue that was chromatographed over a Si gel column (8.00 g, 230−400 mesh) eluted with Me_2CO−toluene (1:99) to give ebelin lactone (13 mg).[2,6]

Peracetylation of Compounds 1−3. Compounds of **1**−**3** (ca. 2 mg each) were peracetylated with Ac_2O-pyridine (0.3 mL, 2:1) and worked up in the usual manner to give the identical peracetylated product **4**: R_f 0.66 [$MeOH-CHCl_3$ (1:9)]; ^{1}H NMR ($CDCl_3$) δ 4.62 (1H, d, J = 6.8 Hz, H-1‴), 4.51 (1H, d, J = 7.5 Hz, H-1″), 4.29 (1H, d, J = 7.9 Hz, H-1′), 3.00 (1H, dd, J = 4.8, 11.4 Hz, H-3), 5.19 (1H, br d, J = 8.2 Hz, H-24), 1.64 (3H, br s, H-26), 1.67 (3H, br s, H-27), 1.15 (3H, s), 1.07 (3H, s), 0.89 (3H, s), 0.80 (3H, s) and 0.72 (3H, s) (5× Me: H-18, H-19, H-21, H-28, and H-29), and 2.10 (3H, s), 2.08 (3H, s), 2.05 (6H, s), 2.00 (3H, s), 1.98 (6H, s), and 1.97 (3H, s) (8× $-OCOCH_3$); FABMS (positive) *m/z* $[M + Na]^+$ 1257.

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Supporting Information Available: ^{1}H and ^{13}C NMR data of colubrin measured in CD_3OD. This material is available free of charge via the Internet at http://pubs.acs.org.

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