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Minor Iridoids from the Roots of *Plumeria acutifolia*[1)]

FUMIKO ABE, RONG-FU CHEN, and TATSUO YAMAUCHI*

Faculty of Pharmaceutical Sciences, Fukuoka University, 8–19–1 Nanakuma, Jonan-ku, Fukuoka 814–01, Japan

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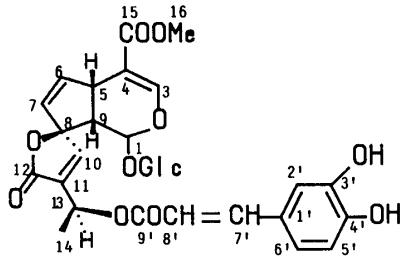
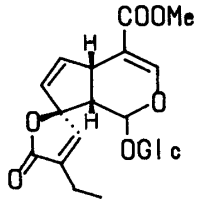
Six new iridoids, *i.e.*, 13-*O*-caffeoylplumieride, 13-deoxyplumieride, β-dihydroplumericinic acid glucosylester, 1α-plumieride, 1α-protoplumericin A, and 8-isoplumieride, were isolated from the polar fraction of the methanol percolate of the roots of *Plumeria acutifolia*. The structures were determined by chemical and spectral methods.

Keywords——*Plumeria*; Apocynaceae; iridoid; plumieride; 8-isoplumieride; 1α-plumieride; 1α-protoplumericin A; β-dihydroplumericinic acid glucosylester; 13-deoxyplumieride

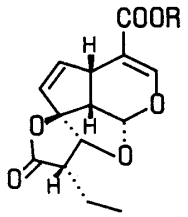
Genus *Plumeria* (Apocynaceae) originates from Central America, and many cultivars are widely distributed in tropical countries. Iridoids from *Plumeria* have been investigated by Schmid and collaborators,[2)] and the structures of six compounds, *i.e.*, plumieride, plumericin, isoplumericin, β-dihydroplumericin (11,13-dihydroplumericin), β-dihydroplumericinic acid, and a yellow pigment, fluvoplumierin, were elucidated initially. Recently we described the isolation and structure determinations of some 13-acylated derivatives of plumieride, 13-*O*-acetylplumieride, protoplumericin A (13-*O*-*p*-*O*-glucosylcoumaroylplumieride), and protoplumericin B (13-*O*-*p*-*O*-glucosylcaffeoylplumieride), together with minor homologues of



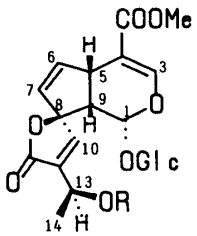
1



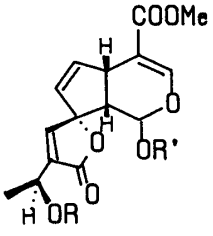
2



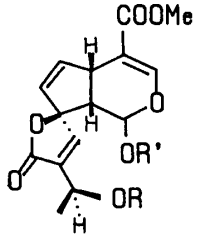
3 : R=Glc
11 : R=Me



4 : R=H
5 : R=*p*-*O*-glucosyl-coumaroyl



6 : R′=Glc, R=H
6-1 : R′=R=H
6-2 : R′=R=Ac



7 : R′=Glc, R=H
7-1 : R′=R=H
8 : R′=Glc
R =coumaroyl
9 : R′=Glc
R =*p*-*O*-glucosyl-coumaroyl

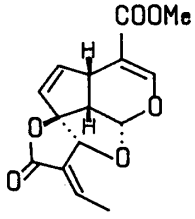


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Chart 1

plumieride and plumericin from *Allamanda neriifolia*.[3] Since then, Coppen and Cobb[4] reported the isolation of protoplumericin A and 13-*O*-coumaroylplumieride from *Plumeria*. We have also investigated the minor iridoids of *Plumeria*, and this paper deals with the isolation and the structure determinations of six new iridoids homologous to plumieride or plumericin from the roots of *Plumeria acutifolia*.

The methanol percolate of the powdered dried roots was fractionated with benzene, $CHCl_3$, and BuOH. The BuOH-soluble fraction was then subjected to chromatographies on a polystyrene column, a silica gel column, and an octadecyl silica (ODS) column, and in the case of some fractions, to high-performance liquid chromatography (HPLC). The minor iridoids, designated as compounds **1**—**6**, were finally isolated together with three known compounds, plumieride (**7**), 13-*O*-coumaroylplumieride (**8**), and protoplumericin A (**9**).

The fast atom bombardment (FAB) mass spectrum (MS) of **1** afforded a molecular peak at *m/z* 655.162, indicating the molecular formula to be $C_{30}H_{32}O_{15}$. In the proton nuclear

TABLE I. ^{13}C Chemical Shifts of Iridoids, δ (ppm) from TMS[a]

	1	**2**	**3**	**4**	**5**	**6**	**7**	**10**[b]	**11**[b]
C-1	93.8	93.8	101.8	93.7	93.6	92.6	94.1	102.8	101.4
C-3	152.1	151.9	154.0	151.7	152.0	151.7	152.0	153.0	152.7
C-4	109.5	109.7	108.4	109.9	109.6	108.3	109.5	109.5	108.5
C-5	40.3	39.8	38.2	39.5	40.0	38.3	40.1	38.8	37.9
C-6	141.6	140.5	141.4	140.1	141.3	141.3	141.0	141.0	141.4
C-7	128.5	130.6	126.9	129.7	128.6	128.6	129.1	127.2	126.1
C-8	96.7	96.3	106.3	96.3	96.6	94.9	96.4	105.0	106.0
C-9	50.3	50.0	53.7	49.9	50.4	46.2	50.0	53.9	53.8
C-10	150.7	148.3	87.0	148.7	151.3	149.3	149.0	80.5	86.7
C-11	133.9	135.0	49.0	139.0	133.6	140.9	138.7	128.3	48.8
C-12	170.2	172.4	176.7	171.2	170.3	171.5	171.3	168.4	176.5
C-13	64.9	18.9	22.8	62.8	65.0	62.9	62.7	144.6	22.7
C-14	19.5	11.8	11.8	22.9	19.2	22.6	23.0	15.8	11.9
C-15	166.6[c]	166.7	165.5	166.6	166.6[c]	166.8	166.7	166.7	166.6
C-16	51.2	51.2		51.1	51.2	51.0	51.2	51.4	51.6
Glc-1	100.6	100.6	95.9	100.7	100.6	101.1	100.8		
					101.7				
Glc-2	74.8	74.7	74.2	74.6	74.8	74.7	74.7		
					74.7				
Glc-3	78.2[d]	78.2[c]	78.6	78.2[c]	78.4[d]	78.3	78.1		
					78.4[d]				
Glc-4	71.5	71.3	71.1	70.9	71.2	71.3	70.8		
					71.2				
Glc-5	79.0[d]	78.8[c]	79.4	78.7[c]	78.9[d]	78.4	78.7		
					78.9[d]				
Glc-6	62.5	62.3	62.2	62.2	62.3	62.7	62.1		
					62.3				
C-1′	126.8				128.9				
C-2′	114.4[e]				130.4				
C-3′	150.6				117.1				
C-4′	147.6				160.2				
C-5′	116.0[e]				117.1				
C-6′	122.2				130.4				
C-7′	146.7				145.3				
C-8′	116.6[e]				116.3				
C-9′	166.5[c]				166.4[c]				

a) Dissolved in pyridine-d_5 unless otherwise mentioned. *b*) Dissolved in $CDCl_3$. *c*—*e*) Signal assignments marked *c*), *d*) or *e*) in each column may be reversed.

TABLE II. ^{1}H Chemical Shifts of Iridoids, δ (ppm) from TMS in Pyridine-d_5 (J/Hz in Parentheses)

	1	2	3	4	5	6[d]	7	10	11
H-1	5.62 (d, 6)	5.64 (d, 5)	5.71 (d, 6)	5.68 (d, 4)	5.66 (d, 5)	5.84[b] (d, 1)	5.60 (d, 6)	5.76 (d, 6)	5.75 (d, 6)
H-3	7.63 (d, 1)	7.65 (d, 1)	7.73 (s)	7.60 (d, 1)	7.60 (d, 1)	7.66 (d, 1)	7.61 (d, 1)	7.58 (s)	7.57 (d, 1)
H-5	3.99 (td, 2, 7)	3.98 (br d, 7)	3.93 (td, 2, 10)	3.97 (ddd, 8, 3, 2)	3.97 (td, 2, 8)	3.80[b] (ddd, 8, 3, 1)	4.00 (ddd, 8, 2, 1)	4.00 (td, 2, 9)	3.94 (td, 2, 9)
H-6	6.43 (dd, 5, 2)	6.46 (dd, 5, 2)	6.14 (dd, 5, 2)	6.47 (dd, 6, 3)	6.48 (dd, 5, 2)	6.68 (dd, 5, 3)	6.46 (dd, 5, 2)	6.08 (dd, 5, 2)	6.09 (dd, 6, 2)
H-7	5.38 (dd, 5, 2)	5.45 (dd, 5, 2)	5.70 (dd, 5, 2)	5.49 (dd, 6, 2)	5.47 (dd, 5, 2)	5.58[c] (dd, 5, 1)	5.41 (dd, 5, 2)	5.77 (dd, 5, 2)	5.77 (dd, 6, 2)
H-9	3.04[a] (dd, 7, 6)	3.07[a] (dd, 7, 5)	3.48 (dd, 10, 6)	3.17[a] (dd, 8, 4)	3.05 (dd, 7, 5)	3.25[a,c] (dd, 8, 1)	3.07[a] (dd, 8, 6)	3.52 (dd, 9, 6)	3.51 (dd, 9, 6)
H-10	7.97[a] (s)	7.41[a] (t, 1)	4.52 (s)	7.81[a] (d, 1)	7.88 (d, 1)	7.50[b] (d, 1)	7.92[a] (d, 1)	5.28 (br s)	4.53 (s)
H-11			2.92 (t, 8)						2.91 (t, 8)
H-13	6.07 (q, 6)	2.21 (m)	1.64 (m) 1.79 (m)	4.96 (q, 6)	6.08 (dq, 1, 7)	4.97 (dq, 1, 7)	4.99 (q, 6)	7.14 (dq, 1, 7)	1.79 (m) 1.70 (m)
H-14	1.61 (d, 6)	1.10 (t, 7)	0.99 (t, 7)	1.63 (d, 6)	1.66 (d, 7)	1.67 (d, 7)	1.63 (d, 6)	1.88 (d, 7)	0.98 (t, 7)
–COOMe	3.63	3.64		3.62	3.63	3.57	3.64	3.71	3.71
Hglc-1	5.39[a] (d, 8)	5.34[a] (d, 8)	6.47 (d, 8)	5.25[a] (d, 8)	5.33 (d, 8) 5.62 (d, 8)	5.21[a] (d, 8)	5.34[a] (d, 8)		
Hglc-2	4.05 (dd, 8, 9)	3.99 (dd, 8, 9)	4.23 (dd, 8, 9)	4.06 (dd, 8, 9)		4.00 (dd, 8, 9)	4.04 (dd, 8, 9)		
Hglc-3	4.26 (t, 9)	4.23 (t, 9)	4.33 (t, 9)	4.21 (t, 9)		4.19 (t, 9)	4.24 (t, 9)		
Hglc-4	4.31 (t, 9)	4.27 (t, 9)	4.36 (t, 9)	4.32 (t, 9)		4.24 (t, 9)	4.35 (t, 9)		
Hglc-5		3.90 (m)	4.10 (m)	3.85 (m)		3.84 (m)	3.88 (m)		
Hglc-6	4.39 (dd, 12, 5) 4.52 (dd, 12, 2)	4.33 (dd, 12, 5) 4.43 (dd, 12, 2)	4.40 (dd, 12, 5) 4.50 (dd, 12, 2)	4.36 (br s)		4.27 (dd, 12, 5) 4.40 (dd, 12, 2)	4.39 (br s)		
Others	6.68 (d, 16, H-8′) 8.02 (d, 16, H-7′) 7.61 (d, 1, H-2′) 7.19 (d, 8, H-5′) 7.17 (dd, 8, 1, H-6′)				6.67 (d, 16, H-8′) 7.94 (d, 16, H-7′) 7.61 (d, 8, H-2′,6′) 7.29 (d, 8, H-3′,5′)				

a—c) Signals marked *a*), *b*) and *c*) responded to irradiation of H-1, H-9 and H-10, respectively, in the differential NOE. *d*) The NOESY spectrum was also measured.

magnetic resonance (^{1}H-NMR) spectrum, the characteristic peaks of plumieride derivatives due to the olefinic protons at C-3 (δ 7.63), C-6 and C-7 (δ 6.43 and δ 5.38), and C-10 (δ 7.97), the carbinyl proton at C-13 (δ 6.07), and methyl protons at C-14 (δ 1.61) were observed besides 1,3,4-trisubstituted benzene proton signals (δ 7.61, 7.19, 7.17) and disubstituted

olefinic proton signals (δ 6.68, 8.02, $J=16$ Hz), assignable to a caffeoyl moiety. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) signals also indicated the presence of a caffeoyl moiety and a plumieride moiety, showing a downfield shift of the 13-carbinyl carbon (+2.2 ppm) and an upfield shift of C-14 (−3.5 ppm). Compound **1** was therefore considered to be 13-*O*-caffeoylplumieride (deglucosyl protoplumericin B). On NaOMe hydrolysis, **1** afforded **7**, while **1** was converted into plumericin (**10**) on hydrolysis with cellulase, as in the case of other 13-acylated plumierides.[3] The structure of **1** was thus confirmed.

Based on the FAB-MS peak at *m/z* 477.138, **2** was found to have one oxygen atom less than **7**, $C_{21}H_{26}O_{11}$. The ^{1}H-NMR spectrum was similar to that of **7**, except that the methyl protons at C-14 were observed as a triplet ($J=7$ Hz) and H-10 was shifted upfield. The C-13 peak in the ^{13}C-NMR spectrum was observed at upper field (−43.8 ppm) as a methylene carbon, as well as C-11 (−3.7 ppm) and C-14 (−11.2 ppm), in a comparison with the corresponding peaks in **7**. The structure of **2** was determined to be 13-deoxyplumieride (allamdin β-D-glucoside).[5]

In the ^{1}H-NMR spectrum of **3**, no proton signal due to the 4-carbomethoxyl group was observed. Based on the ^{1}H–^{1}H COSY spectrum, the peaks of H-5, H-6, H-7, and H-9 in the iridoid framework were confirmed together with the presence of one ethyl group. All the carbon signals of **3** were assigned by ^{13}C–^{1}H COSY and the signals of C-8—C-14 showed similar chemical shifts to those of β-dihydroplumericin (**11**).[2,6] Since the H-10 signal was seen as a singlet, the orientation of H-11 is β and the ethyl moiety retains α-orientation.[5,7] The signals due to one glucosyl moiety were assignable in the ^{13}C-NMR spectrum, and the anomeric proton signal at lower field (δ 6.47, d, $J=8$ Hz) suggested that the glucose forms an ester with the carboxyl residue. Compound **3** was therefore determined to be β-dihydroplumericinic acid glucosyl ester and is named plumenoside.

Compound **4** has the same molecular formula as **7**, and **4** showed a longer retention time than **7** in HPLC. The ^{1}H- and ^{13}C-NMR signals showed similar patterns to those of **7** with slight shifts of H-1 (+0.08 ppm), H-7 (+0.08 ppm), H-9 (+0.10 ppm), and H-10 (−0.11 ppm). Compound **5** showed the same molecular formula as **9**, and the similarity of the ^{1}H- and ^{13}C-NMR spectra to those of **9** suggesting a 13-*O*-*p*-*O*-glucosylcoumaroyl residue, which was removed with NaOMe to afford **4**. When **5** was subjected to hydrolysis with cellulase, the product was proved to be **10** as shown in the hydrolysis of **9**,[3] indicating that **4** and **5** retain the same structures as **7** and **9**, respectively, except for the stereochemistry at C-1. The structures of **4** and **5** were therefore determined to be 1α-plumieride and 1α-protoplumericin A, respectively. When H-1α of **1**, **2** or **7** was irradiated in differential nuclear Overhauser effect (NOE) measurements, responses were observed at H-9 and H-10, as well as H-1′ in each compound. The H-1α is therefore considered to retain equatorial configuration as in allamdin, an aglycone of **2** (determined by X-ray analysis).[5] In **4**, H-1 also showed the responses at H-9 and H-10 but not H-5, supporting the hypothesis that H-1β retains equatorial configuration with the downward orientation of the glucosyloxy residue.

Compound **6** has the same molecular formula as **7** and **4**, and showed an intermediate retention time between **7** and **4** on HPLC. The component sugar was determined to be glucose, based on the ^{13}C-NMR spectrum. On enzymic hydrolysis, **6** afforded an aglycone (**6**-1) and acetylation of **6**-1 provided a diacetate (**6**-2) as in the case of an aglycone of **7** (**7**-1), indicating the presence of two acylable hydroxyl groups. In a comparison of the NMR spectra of **6** and **7**, the coupling constants between H-5/H-6, H-6/H-7, and H-5/H-9 were the same as those of **7**, suggesting the configuration at C-5 and C-9 to be *cis* as in **7**. An upfield shift was seen in H-10 (−0.42 ppm) while H-1, H-6, and H-7 were shifted downfield. In the ^{13}C-NMR spectrum, upfield shifts were observed in C-1 (−1.5 ppm), C-5 (−1.8 ppm), C-8 (−1.5 ppm) and C-9 (−3.8 ppm), and C-11 was shifted downfield (+2.2 ppm). All carbon signals corresponding to the proton signals were assigned from the ^{13}C–^{1}H COSY spectrum. On the

basis of the chemical and spectral considerations, **6** seemed to be an isomer of **7** having a reversed sterochemistry at C-8.

In order to confirm this supposition, circular dichroism (CD) and NOESY measurements were carried out. In the CD spectra, **7** showed a positive maximum at 266 nm, while **6** afforded a negative maximum at 261 nm. In the NOESY of **6**, cross peaks were observed between H-9/H-10, and H-1/H-9, as well as H-9/H-5 and H-10/H-7, indicating that the linkage between C-8 and C-10 is β, a reversed C-8 configuration from the normal plumieride homologues, and equatorial conformation of H-1. The unusually small coupling constant of H-1 in **6** ($J=1$ Hz) can be explained by the expansion of the dihedral angle between H-1α and H-9 to approximately 90°, as a result of deformation of the dihydropyran ring due to the approach of the two oxygen atoms at C-1 and C-8. The downfield shift of H-1 seems to be caused by the location of H-1α in close proximity to the C-8 oxygen. The stereochemistry at C-13 is tentatively assigned to be *S*, the same as that of **7**, since the same four-carbon unit seems to be attached at C-10 of the intermediate when **6** is biosynthesized. Compound **6** is thus determined to be the isomer of **7** at C-8, and is named 8-isoplumieride.

The structures of six minor iridoids in the polar fraction, having a characteristic framework homologous to plumieride or plumericin, were thus established. The benzene fraction in the partition of the MeOH percolate mainly contains **10** and the results of a study on the minor components of this fraction will be published elsewhere.

Experimental

Melting points were taken on a hot stage apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-360. Ultraviolet (UV) spectra were taken in MeOH on a Shimadzu 200S double-beam spectrophotometer. CD spectra were taken on a JASCO J-20 spectro-polarimeter. The samples for ^{1}H- and ^{13}C-NMR spectroscopy were dissolved in pyridine-d_5 unless otherwise mentioned and measured on a JEOL GX-400 or a Hitachi R-22 (90 MHz). Chemical shifts are given in δ values referred to internal tetramethylsilane (TMS), and the following abbreviations are used; s=singlet, br s=broad singlet, d=doublet, dd=doublet of doublets, br d=broad doublet, t=triplet, td=triplet of doublets, q=quartet, dp=doublet of quartets, m=multiplet. FAB-MS were recorded on a JEOL D-300-FD spectrometer. HPLC was run on a Waters model ALC 200 equipped with radial pack C_{18} column. For silica gel chromatography, thin layer chromatography (TLC), and droplet counter current chromatography (DCCC), the following solvent systems were employed: solv. 1, $CHCl_3$–MeOH–H_2O (bottom layer); solv. 2, EtOAc–MeOH–H_2O (top layer); solv. 3, benzene–acetone; solv. 4, hexane–EtOAc. Spots on TLC plates were visualized by spraying with diluted H_2SO_4 and heating the plate.

Extraction and Isolation——Dried powdered roots of *Plumeria acutifolia* (6 kg), planted and grown in Taipei, Taiwan, were percolated with MeOH. The MeOH percolate was concentrated *in vacuo* and the deposit was filtered off. The deposit showed a spot with the same *Rf* value as **10** on TLC and was not investigated further. The filtrate was diluted with H_2O in order to adjust the concentration of MeOH to *ca.* 50% and again the deposit showing a spot with the same *Rf* value as **10** on TLC was filtered off. The filtrate was extracted with benzene (ext. 45 g) and then with $CHCl_3$ (36.5 g). The benzene and the $CHCl_3$ extracts showed the presence of **10** and **8** on TLC, respectively.

After $CHCl_3$ extraction, the H_2O layer was concentrated *in vacuo* in order to remove MeOH, and the residue was extracted with BuOH. The BuOH extract (312 g) was fractionated on an MCI-gel column (Mitsubishi Chem. Co., CHP-20P) with a solvent sytem of H_2O–MeOH, gradually increasing the MeOH concentration to 100%.

The eluate with 60% MeOH (ext. 56 g) contained principally **8**. The eluate was further chromatographed on a silica gel column with solv. 1 (7:2:1.2—7:3:1) to afford **8** (43 g). The following fraction containing **1** (ext. 200 mg) was further fractionated on a silica gel column with solv. 2 (6:1:5) to afford **1** (60 mg). The eluates with 20% and 30% MeOH were combined (ext. 28 g) and chromatographed on a silica gel column with solv. 1 (7:2:1—7:3:1.6) to afford fractions containing **2** and **3** (5 g, fr. 1), **7** (7.5 g, fr. 2), and **7** and **6** (30 g, fr. 3). Fraction 1 was further chromatographed on a silica gel column with solv. 2 (5:1:3—5:1:2) and again on a silica gel column with solv. 1 (7:1:1.2—7:1:1) to afford **2** (300 mg) and **3** (50 mg). Compounds **2** and **3** were further purified by DCCC (solv. 1, 4:6:5, ascending) to afford a homogeneous solid. Fraction 3 was again chromatographed on a silica gel column with solv. 1 (7:2:1) and then on an ODS column with 12—14% CH_3CN to afford crude **6**. Compound **6** was further purified by DCCC (solv. 1, 4:6:5, ascending), followed by crystallization from MeOH to give a crystalline powder (700 mg), showing a single peak in HPLC (solv., 22% CH_3CN).

The mother liquor from the crystallization of **7** (fr. 2) from MeOH showed an unknown peak in HPLC. The fraction was further chromatographed on an ODS column with 12—14% CH_3CN and then purified by HPLC (solv.

22% CH_3CN) to afford **4** as a homogeneous solid (20 mg) showing a single peak in HPLC and a single spot on TLC.

The eluates with 40% and 50% MeOH on an MCI-gel column (ext. 24 g) showed the presence of **9**, and were further purified on a silica gel column with solv. 1 (7 : 2 : 1—7 : 3 : 1.6—7 : 3 : 1.2) to afford **9** (*ca.* 9 g), as a mixture of *trans* and *cis* derivatives of the *p*-coumaric acid moiety based on the ^{1}H-NMR spectrum. On ODS column chromatography of **9** with 16—20% CH_3CN, *trans*-**9** was eluted faster than *cis*-**9**, although separation was not complete. The final fraction on an ODS column was further subjected to HPLC with 26% CH_3CN to afford **5** (20 mg).

13-*O*-Caffeoylplumieride (1)——A solid, $[\alpha]_D^{25}$ −60.0° (c=1.00, MeOH). UV λ_{max} nm (log ε): 205 (4.50), 220 (4.44), 300 (sh) (3.96), 323 (4.05). FAB-MS *m/z*: 655.162 (Calcd for $C_{30}H_{32}O_{15}$+Na: 655.164), 537, 237, 163. A solution of NaOMe in MeOH (0.05 ml, prepared from 0.5 g of Na and 20 ml of MeOH) was added to a solution of **1** in MeOH (5 mg/0.6 ml), and the mixture was allowed to stand at room temperature for 1 h. The mixture was then diluted with MeOH and neutralized with IR-120B, and the MeOH was evaporated off *in vacuo*. The residue was run in parallel with **7** on TLC (solv. 1, 7 : 3 : 1; solv. 2, 4 : 1 : 0.5). The two samples showed the same *Rf* values. Compound **1** (5 mg) was dissolved in 25% EtOH and was shaken with 10 mg of cellulase (Sigma Co.) at 38 °C for 20 h. The mixture was diluted with H_2O and extracted with BuOH. The BuOH extract showed the same *Rf* values as **10** in TLC (solv. 3, 10 : 1; solv. 4, 2 : 1).

13-Deoxyplumieride (2)——Crystalline powder from dilute EtOH, mp 129—131 °C, $[\alpha]_D^{25}$ −113.6° (c=1.50, MeOH). UV λ_{max} nm (log ε): 213 (4.27), 238 (sh), (4.06). FAB-MS *m/z*: 477.138 (Calcd for $C_{21}H_{26}O_{11}$+Na: 476.137), 293, 275.

Plumenoside (β-Dihydroplumericinic Acid Glucosylester) (3)——A solid, $[\alpha]_D^{25}$ +117.3° (c=1.54, MeOH). UV λ_{max} nm (log ε): 238 (4.10). FAB-MS *m/z*: 463.122 (Calcd for $C_{20}H_{24}O_{11}$+Na: 463.122).

1α-Plumieride (4)——A solid, $[\alpha]_D^{25}$ −46.4° (c=1.30, MeOH). UV λ_{max} nm (log ε): 205 (4.26). FAB-MS *m/z*: 493.136 (Calcd for $C_{21}H_{26}O_{12}$+Na: 493.132). HPLC (20% CH_3CN, 1 ml/min): t_R 8.4 min (**7**: 6.0 min).

1α-Protoplumericin A (5)——A solid, $[\alpha]_D^{30}$ −44.1° (c=1.00, MeOH). UV λ_{max} nm (log ε): 205 (4.53), 220 (4.45), 295 (4.03), 305 (4.03). FAB-MS *m/z*: 801 ($C_{36}H_{42}O_{19}$+Na), 585, 273. On alkaline hydrolysis of **5** (5 mg) with NaOMe/MeOH in the same manner as described for **1**, the product was identified as **4** by TLC (solv. 1, 7 : 3 : 1) and HPLC in parallel. Compound **5** (5 mg) was hydrolyzed with cellulase in the same manner as described for **1**. The BuOH extract showed the same *Rf* value as **10** in TLC (solv. 3, 10 : 1, solv. 4, 2 : 1).

8-Isoplumieride (6)——mp 168—173 °C, $[\alpha]_D^{20}$ −164.8° (c=0.75, MeOH). CD (c=0.12, MeOH) $[\theta]^{25}$ (nm): −5200 (262) (negative maximum) (CD of **7** (c=0.10, MeOH) $[\theta]^{25}$ (nm): +1057 (266) (positive maximum)). UV λ_{max} nm (log ε): 210 (4.20), 230 (sh), (4.07). FAB-MS *m/z*: 493.133 (Calcd for $C_{21}H_{26}O_{12}$+Na; 493.132). HPLC (20% CH_3CN, 1 ml/min): 7.8 min (**7**: 6.0 min). The acetate of **6** was obtained by usual acetylation as a solid, $[\alpha]_D^{26}$ −148.2° (c=3.22, MeOH). FAB-MS *m/z*: 703.187 (Calcd for $C_{31}H_{36}O_{17}$+Na; 703.185). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 7.05 (1H, d, J=2 Hz, H-3), 6.60 (1H, dd, J=6, 2 Hz, H-6), 5.44 (1H, dd, J=6, 2 Hz, H-7), 2.91 (1H, br d, J=9 Hz, H-9), 7.35 (1H, d, J=2 Hz, H-10), 5.62 (1H, dq, J=2, 6 Hz, H-13), 1.50 (3H, d, J=6 Hz, H-14), 3.72 (3H, s, $-COOCH_3$), 2.09, 2.06, 2.02, 1.99, 1.91 (3H each, s, –OAc). Compound **6** (150 mg) was dissolved in 20% EtOH (5 ml) and the solution was shaken with cellulase (200 mg) for 20 h at 38 °C. The mixture was extracted with BuOH. The BuOH extract was purified on a silica gel column with solv. 1 (7 : 1 : 1.2) to give a solid with one homogeneous spot on TLC (**6**-1, 18 mg). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 5.13 (1H, d, J=4 Hz, H-1), 7.16 (1H, d, J=2 Hz, H-3), 6.46 (1H, dd, J=6, 3 Hz, H-6), 5.43 (1H, dd, J=6, 2 Hz, H-7), 7.43 (1H, d, J=1 Hz, H-10), 1.44 (3H, d, J=6 Hz, H-14). Compound **6**-1 (10 mg) was acetylated with pyridine and Ac_2O at room temperature. The acetate of **6**-1 (**6**-2) was obtained as a solid, $[\alpha]_D^{20}$ −84.2° (c=0.55, MeOH). Electron impact (MS) *m/z*: 392.111 (Calcd for $C_{19}H_{20}O_9$: 392.111). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 5.90 (1H, d, J=2 Hz, H-1), 7.00 (1H, d, J=2 Hz, H-3), 6.40 (1H, dd, J=5, 2 Hz, H-6), 5.42 (1H, dd, J=5, 2 Hz, H-7), 2.76 (1H, dd, J=4, 8 Hz, H-9), 7.34 (1H, d, J=2 Hz, H-10), 5.61 (1H, dq, J=2, 6 Hz, H-13), 1.50 (3H, d, J=6 Hz, H-14), 3.72 (3H, s, $-COOCH_3$), 2.09 (6H, s, 2 × OAc).

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References and Notes

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