Tareciliosides H—M: Further Cycloartane Glycosides from Leaves of *Tarenna gracilipes*

Zhimin Zhao,[a] Katsuyoshi Matsunami,[a] Hideaki Otsuka,*[,a] Takakazu Shinzato,[b] and Yoshio Takeda[c]

[a] *Department of Pharmacognosy, Graduate School of Biomedical Sciences, Hiroshima University; 1–2–3 Kasumi, Minami-ku, Hiroshima 734–8553, Japan:* [b] *Subtropical Field Science Center, Faculty of Agriculture, University of the Ryukyus; 1 Senbaru, Nakagami-gun, Okinawa 903–0213, Japan: and* [c] *Faculty of Pharmacy, Yasuda Women's University; 6–13–1 Yasuhigashi, Asaminami-ku, Hiroshima 731–0153, Japan.*

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From the 1-BuOH-soluble fraction of a MeOH extract of leaves of *Tarenna gracilipes*, collected in Okinawa, six further new cycloartane glycosides, named tareciliosides H—M (1—6), were isolated. Their structures were established through a combination of spectroscopic analyses.

Key words *Tarenna gracilipes*; Rubiaceae; tarecilioside; cycloartane glycoside

In a preceding paper,[1)] we reported the isolation and characterization of seven cycloartane glycosides, tareciliosides A—G, from the 1-BuOH-soluble fraction of a MeOH extract of the leaves of *Tarenna gracilipes*. Further detailed investigation of the 1-BuOH-soluble fraction has resulted in the isolation of six additional cycloartane glycosides, named tareciliosides H—M (**1**—**6**). In this paper, we report the isolation and structural elucidation of the six new cycloartane glycosides.

Results and Discussion

The 1-BuOH-soluble fraction of MeOH extract of the leaves of *T. gracilipes*[1)] was subjected to a column of Diaion HP-20, using MeOH–H_2O mixtures, to give seven fractions. Fractions 14—19 were further subjected to silica gel column chromatography (CC), using a $CHCl_3$–MeOH–H_2O solvent system with increasing polarity. The fractions eluted from these columns were combined and subjected to octadecylsilanized silica gel (ODS) CC, droplet counter-current chromatography (DCCC), and HPLC, successively, to afford tareciliosides H—M (**1**—**6**).

Tarecilioside H (**1**), $[\alpha]_D^{25}$ −15.5, was isolated as an amorphous powder and its molecular formula was determined to be $C_{42}H_{72}O_{14}$ on positive-ion high-resolution (HR)-electrospray ionization (ESI)-time-of-flight (TOF)-MS. The strong absorption band at 3408 cm^{-1} in the IR spectrum indicated the presence of sugar moiety. The ^{1}H-NMR spectrum of tarecilioside H (**1**) (Table 1) showed two highly shielded signals, characteristic of methylene protons of a cyclopropane ring as an AX system (δ_H 0.21, 0.77, each d, J=4 Hz, H_2-19), and signals due to six singlet methyls (δ_H 1.12, 1.23, 1.28, 1.46, 1.48, 1.50) and two secondary methyl [δ_H 1.13, (d, J=7 Hz) and 1.68 (d, J=6 Hz)] groups. Additionally, the resonances for two anomeric protons were observed at δ_H 4.92 (d, J=8 Hz) and 6.50 (s). Thus, tarecilioside H (**1**) was considered to be a cycloartane-type triterpene diglycoside analogous to tarecilioside A.[1)] This assumption was supported by the ^{13}C-NMR spectral data for **1** (Table 2). The ^{13}C-NMR spectrum of **1** exhibited the signals of 42 carbons, of which 30 accounted for an aglycone moiety. The remaining signals were in good accordance with the presence of two sugar units. The resonances assigned to the aglycone moiety were essentially the same as those of tarecilioside A.[1)] The anomeric proton of the glucose unit (δ_H 4.92, d, J=8 Hz), which showed a long-range correlation with C-3 (δ_C 88.3) of the aglycone moiety, confirmed the position of the glucose linkage. The anomeric proton of the rhamnose unit (δ_H 6.50, s) also exhibited a long-range correlation with C-2′ (δ_C 77.9) of the glucose unit, which confirmed the attachment of a rhamnose unit to the hydroxy group at C-2′ of glucose. The configuration of the C-24 hydroxy group was indicated to be 24*R* on comparison with the chemical shift values of cyclounifolioside C (24*R*, C-24: δ_C 80.3),[2)] cyclocantogenin (24*S*, C-24: δ_C 70.0),[2)] oleifoliosides A and B (24*S*, C-24: 77.1),[3)] and tarecilioside A (24*R*, C-24: δ_C 80.6).[1)] Acid hydrolysis of **1** gave D-glucose and L-rhamnose. Additionally, the coupling constant (δ_H 4.92, d, J=8 Hz) for one (H-1′) of the anomeric protons for D-glucopyranose indicated that the mode of linkage was β and that for another anomeric proton (H-1″) for L-rhamnopyranose at δ_H 6.50 (s) was indicated to be α. Therefore, the structure of tarecilioside H (**1**) was elucidated to be 2′-*O*-α-L-rhamnopyranosyl tarecilioside A, as shown in Fig. 1.

Tarecilioside I (**2**), $[\alpha]_D^{25}$ −10.3, was isolated as an amorphous powder and its molecular formula was determined to be $C_{47}H_{80}O_{18}$ on positive-ion HR-ESI-TOF-MS. All of the assignments of the proton and carbon signals for tarecilioside I, confirmed by the correlation spectroscopy (COSY), heteronuclear single quantum coherence (HSQC), and heteronulear multiple bond correlation (HMBC) spectra, and comparison of these data with those for tarecilioside H (**1**) indicated similarity to **1**. A difference between **1** and **2** was that the ^{13}C-NMR spectrum of **2** contained five more signals than that of **1**, which was in good accordance with the presence of one xylopyranose unit. In the HMBC spectrum of **2**, the long range correlation between the anomeric proton of the xylopyranose unit (δ_H 5.04, d, J=8 Hz) and C-25 (δ_C 80.9) of the aglycone moiety indicated the position of the xylopyranose linkage. On acid hydrolysis of **2**, D-glucose, L-rhamnose and D-xylose were obtained. The glucopyranose linkage was located at the hydroxy group at C-3 in the β-mode, since HMBC long-range correlation of the glucose anomeric proton (δ_H 4.91, d, J=8 Hz) with C-3 (δ_C 88.3) was observed. On the other hand, the anomeric proton of the

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

Table 1. ^{1}H-NMR Spectral Data for Tareciliosides H—M (**1**—**6**) (400 MHz, Pyridine-d_5)[a)]

H	1	2	3	4[b)]	5	6
1	1.20 m	1.32 m	1.21 m	1.16 m	1.10 m	1.18 m
	1.40 m	1.54 m	1.50 m	1.45 m	1.45 m	1.45 m
2	1.86 m	1.85 m	1.83 m	1.90 m	1.87 m	1.92 m
	2.38 m	2.41 m	2.40 m	2.35 m	2.38 m	2.36 m
3	3.47 dd, 11, 4	3.52 dd 12, 4	3.46 dd 12, 4	3.43 dd, 11, 4	3.40 dd 12, 4	3.44 dd 12, 4
5	1.55 dd 10, 2	1.55 m	1.48 m	1.53 m	1.26 m	1.51 m
6	1.20 m	1.20 m	1.20 m	1.26 m	0.72 m	1.12 m
	2.02 m	1.97 m	1.95 m	2.02 m	1.53 m	1.90 m
7	3.76 d-like 10	3.78 ddd 10, 10, 4	3.75 m	3.77 ddd 9, 9, 4	1.04 m	3.72 ddd 10, 10, 4
					1.27 m	
8	2.04 d 10	2.04 d 10	2.01 d 10	2.01 d 9	1.63 m	1.80 d 10
11	1.39 m	1.34 m	1.23 m	1.22 m	1.05 m	1.44 m
	1.89 m	1.84 m	1.84 m	1.85 m	1.92 m	1.98 m
12	1.64 2H m	1.64 2H m	1.62 2H m	1.60 m	1.60 2H m	1.73 2H t 7
				1.68 m		
15	2.31 dd, 13, 3	2.30 dd 14, 4	2.28 dd, 14, 4	2.31 dd 14, 4	1.67 m	2.66 d 19
	2.72 dd 13, 8	2.71 dd 14, 8	2.70 dd 14, 8	2.74 dd, 14, 8	2.06 dd 13, 8	2.72 d 19
16	4.74 m	4.71 m	4.73 m	4.74 m	4.65 m	
17	1.81 d-like 10	1.79 dd 11, 8	1.74 dd 11, 8	1.75 dd, 11, 7	1.72 dd 11, 7	2.35 d 7
18	1.46 s	1.48 s	1.41 s	1.44 s	1.34 s	1.21 s
19	0.21 d 4	0.21 d 4	0.19 d 4	0.21 d 4	0.20 d 4	0.28 d 4
	0.77 d 4	0.77 d 4	0.75 d 4	0.75 d 4	0.52 d 4	0.71 d 4
20	2.35 m	2.34 m	2.18 m	2.20 m	2.18 m	1.96 m
21	1.13 d 7	1.11 d 6	1.02 d 6	1.05 d 7	1.00 d 6	1.05 d 6
22	2.42 m	2.42 m	1.83 m	1.53 m	1.87 m	1.90 m
	2.51 m	2.49 m	2.40 m	2.40 m	2.38 m	2.52 m
23	1.81 m	1.62 m	3.15 ddd 18, 8, 8	3.09 ddd 17, 10, 6	3.12 ddd 18, 8, 8	3.04 m
	2.10 m	1.98 m	3.28 m	3.16 ddd 18, 8, 8	3.27 ddd 18, 8, 8	3.11 m
24	3.78 d-like 10	3.86 dd 10, 2				
26	1.50 s	1.49 s	1.54 s	1.50 s	3.95 d 10	1.55 s
					4.20 m	
27	1.48 s	1.49 s	1.56 s	1.52 s	1.49 s	1.57 s
28	1.28 s	1.28 s	1.27 s	1.35 s	1.32 s	1.34 s
29	1.23 s	1.23 s	1.22 s	1.19 s	0.16 s	1.20 s
30	1.12 s	1.12 s	1.09 s	1.11 s	0.88 s	1.20 s
1′	4.92 d 8	4.91 d 8	4.90[b)]	4.93 d 8	4.89 d 7	4.93 d 8
2′	4.27 m	4.26 m	4.26 m	4.26 m	4.23 m	4.26 m
3′	4.25 m	4.24 m	4.26 m	4.26 m	4.23 m	4.26 m
4′	4.10 m	4.12 m	4.10 m	4.27 m	4.25 m	4.23 m
5′	3.90 m	3.91 m	3.89 m	4.01 m	3.96 m	4.02 m
6′	4.33 dd 12, 5	4.33 dd 12, 6	4.32 dd 12, 5	4.43 dd 11, 4	4.42 dd 11, 4	4.43 dd 11, 5
	4.50 dd 12, 2	4.51 dd 12, 3	4.50 dd 12, 2	4.72 dd 11, 2	4.72 dd 11, 2	4.73 dd 11, 3
1″	6.50 s	6.50 s	6.50 s	5.30 d 8	5.29 d 8	5.32 d 8
2″	4.80 m	4.81 m	4.81 m	4.06 m	4.03 m	4.04 m
3″	4.62 m	4.62 m	4.62 dd 7, 3	4.15 m	4.19 m	4.20 m
4″	4.30 m	4.26 dd 9, 9	4.15 m	4.16 m	4.10 m	4.13 m
5″	4.76 m	4.77 m	4.79 m	3.87 m	3.80 m	3.88 m
6″	1.68 d 6	1.68 d 6	1.68 d 6	4.33 dd 12, 5	4.26 m	4.34 m
				4.49 dd 12, 2	4.47 dd 11, 4	4.49 dd 11, 3
1‴		5.04 d 8	4.95 d 8	5.08 d 8	5.06 d 8	5.09 d 8
2‴		3.93 dd 8, 8	4.04 m	4.03 m	4.00 m	4.03 m
3‴		4.24 m	4.20 m	4.30 m	4.27 m	4.25 m
4‴		4.09 m	4.17 m	4.21 m	4.16 m	4.25 m
5‴		4.21 m	3.79 m	3.94 m	3.90 m	3.94 m
		3.68 dd 10, 10				
6‴			4.27 m	4.33 dd 12, 5	4.31 dd 11, 5	4.43 m
			4.40 dd 12, 3	4.40 dd 12, 3	4.47 dd 11, 3	4.49 dd 11, 3

a) Assigments were performed by means of COSY, HSQC, HMQC and HMBC experiments. *b)* In the DHO envelope. m: multiplet or overlapped signal.

rhamnose unit (δ_H 6.50, s) exhibited a long-range correlation with C-2′ (δ_C 77.9) of the glucosee unit, which confirmed the attachment of the rhamnose unit to the hydroxy group at C-2′ of glucose. Therefore, the structure of tarecilioside I (**2**) was elucidated to be 25-*O*-β-D-xylopyranosyl tarecilioside H, as shown in Fig. 1.

Tarecilioside J (**3**), $[\alpha]_D^{25}$ −18.8, was isolated as an amorphous powder and its molecular formula was determined to be $C_{48}H_{80}O_{19}$ on positive-ion HR-ESI-TOF-MS. Tarecilioside J (**3**) was an cycloartane triglycoside analogous to tarecilioside I (**2**) and tarecilioside F.[1)] In the downfield region of the ^{13}C-NMR spectrum of **3**, a highly deshielded signal at δ_C 215.4 was expected to represent an isolated ketone functional group, and its location was determined to be C-24, judging

Table 2. ^{13}C-NMR Spectral Data for Tareciliosides H—M (**1**—**6**) (100 MHz, Pyridine-d_5)

C	1	2	3	4[a)]	5	6
1	32.0	32.0	30.9	31.9	32.2	31.9
2	30.0	29.9	29.9	29.8	30.4	29.7
3	88.3	88.3	88.3	88.8	89.0	88.7
4	41.0	41.0	40.9	41.0	41.4	41.1
5	46.5	46.5	46.5	46.5	47.7	46.7
6	32.0	32.0	32.0	32.0	21.1	31.92
7	70.3	70.3	70.3	70.4	26.3	70.3
8	55.1	55.1	55.1	55.2	48.1	54.7
9	20.1	20.1	20.1	20.2	19.9	19.3
10	26.9	26.9	26.9	27.0	26.4	27.26
11	26.8	26.8	26.8	26.8	26.5	26.2
12	33.2	33.2	33.1	33.2	33.3	31.6
13	46.1	46.1	46.2	46.2	45.7	45.9
14	47.1	47.1	47.0	47.1	47.2	41.9
15	50.7	50.6	50.4	50.5	48.5	54.1
16	72.2	72.2	72.2	72.1	71.7	219.9
17	56.8	56.8	56.9	56.8	57.4	61.2
18	18.7	18.7	18.4	18.8	19.3	19.13
19	28.5	28.5	28.5	28.6	29.9	29.8
20	31.6	31.6	30.5	30.5	30.4	31.7
21	18.9	18.9	18.7	18.3	18.1	19.4
22	35.0	35.0	30.0	30.5	30.0	30.0
23	29.4	29.3	34.4	34.1	35.7	34.5
24	80.6	79.1	215.4	217.9	217.7	216.3
25	72.7	80.9	82.9	76.9	80.0	76.8
26	25.7	21.1	23.7	27.2	69.2	27.26
27	26.1	24.2	24.7	27.3	22.5	27.27
28	25.9	25.7	25.7	26.0	26.0	25.9
29	15.5	15.5	15.5	15.4	15.5	15.5
30	20.0	20.0	20.0	20.1	20.3	19.15
1′	105.2	105.2	105.2	104.8	104.9	104.8
2′	77.9	77.9	77.9	82.9	83.0	82.9
3′	79.9	79.9	79.9	78.35	78.4	78.4
4′	72.0	72.0	72.1	71.8	71.8	71.8
5′	78.1	78.1	78.1	77.7	77.1	77.1
6′	62.9	63.0	62.9	70.2	70.1	70.2
1″	101.7	101.7	101.7	105.6	105.6	105.6
2″	72.4	72.4	72.4	76.8	76.7	76.5
3″	72.5	72.5	72.5	78.3	78.3	78.0
4″	74.1	74.1	74.1	71.8	71.7	71.8
5″	69.9	69.6	69.6	77.9	77.9	77.97
6″	18.7	18.7	18.7	62.8	62.8	62.8
1‴		99.4	99.6	105.3	105.3	105.3
2‴		75.2	75.3	75.3	75.3	75.3
3‴		78.6	78.7	78.3	78.3	78.3
4‴		71.1	71.7	71.6	71.6	71.6
5‴		67.0	78.2	78.3	78.0	78.0
6‴			62.8	62.9	62.9	62.9

a) Data for 150 MHz.

from the result of analysis of the HMBC and ^{1}H–^{1}H COSY spectra of **3** and comparison with tarecilioside F.[1)] The other difference between **2** and **3** was expected to be the sugar unit linked at C-25. On analysis of the ^{13}C-NMR spectrum of **3**, the xylopyranose in **2** was expected to be replaced by glucopyranose in **3**. On acid hydrolysis of **3**, only D-glucose and L-rhamnose were obtained. The positions of sugar linkages were also the same as those in **2**, and one glucopyranose was also located at the hydroxy group at C-25 in the β-mode, since in the HMBC spectrum, long-range correlations of anomeric proton H-1′ (δ_H 4.90) with C-3 (δ_C 88.3), H-1″ (δ_H 6.50) with C-2′ (δ_C 77.9), and H-1‴ (δ_H 4.95) with C-25 (δ_C 82.9) were observed, although H-1′ (δ_H 4.90) and H-1‴ (δ_H 4.95) were overlapped by a huge water signal. Therefore, the

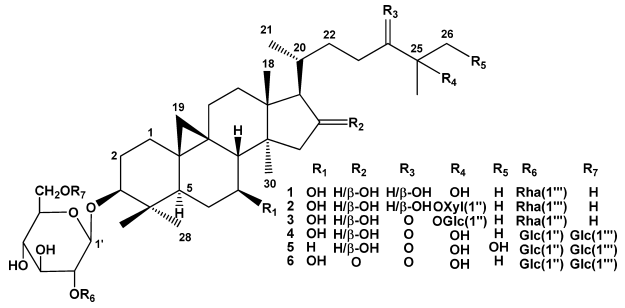

Fig. 1. Structures of Isolated Compounds

structure of tarecilioside J (**3**) was elucidated to be 2′-*O*-α-L-rhamnopyranosyl tarecilioside F, as shown in Fig. 1.

Tarecilioside K (**4**), $[\alpha]_D^{25}$ −5.96, was isolated as an amorphous powder and its molecular formula was determined to be $C_{48}H_{80}O_{20}$ on positive-ion HR-ESI-TOF-MS. Analysis and comparison of the HMBC and ^{1}H–^{1}H COSY spectra, tarecilioside K (**4**) was also found to be a cycloartane triglycoside analogous to tarecilioside J (**3**), except for the sugar varieties and the positions of attached sugar units. On acid hydrolysis, only D-glucose was detected as a sugar component. However, one of the glucoses was not at the hydroxy group at C-25, but at the 2′-position of the other glucose moiety, which was attached at C-3 of the aglycone. The third glucose moiety was attached at C-6′ of the glucose, which attached at the C-3. All of these attachments were confirmed by the HMBC experiment, since long-range correlations of glucose anomeric protons H-1′ (δ_H 4.93) with C-3 (δ_C 88.8), H-1″ (δ_H 5.30) with C-2′ (δ_C 82.9), and H-1‴ (δ_H 5.08) with C-6 (δ_C 70.2) were observed. The glucosylation shift trend also supported the above observations when the ^{13}C-NMR spectra of tarecilioside K (**4**) and tarecilioside F were compared, the C-2′ carbon signal being shifted downfield by 7.1 ppm, the C-1′ anomeric carbon being shifted upfield by 2 ppm and on the other hand, the C-6′ carbon signal being shifted downfield by 7.1 ppm. Therefore, the structure of tarecilioside K (**4**) was elucidated to be 6′-*O*-β-D-glucopyranosyl tarecilioside G.

Tarecilioside L (**5**), $[\alpha]_D^{25}$ +1.19, was isolated as an amorphous powder and its molecular formula was determined to be $C_{48}H_{80}O_{20}$ on positive-ion HR-ESI-TOF-MS. The signals observed in the^{1}H- and ^{13}C-NMR spectra of tarecilioside L (**5**) were very similar to those of tarecilioside K (**4**), except for the position of one hydroxy functional group. On analysis of the ^{13}C-NMR spectrum of **5**, the methine signal at δ_C 70.4, which was observed in the ^{13}C-NMR spectrum of **4**, was displaced by a methylene group at δ_C 26.3 and one oxymethylene signal was observed at δ_C 69.2. In the ^{1}H–^{1}H COSY spectrum of **5**, proton H-5 (δ_H 1.26) showed correlation with H_2-6 (δ_H 0.72, 1.53), while H_2-6 showed cross peaks with H_2-7 (δ_H 1.04, 1.27), thus all of these correlations indicated that the C-7 hydroxy functional group was absent in **5**. On the other hand, in the NMR spectrum of **5**, only five tertiary methyl carbons were observed with a new primary alcohol signal [δ_C 69.2 with δ_H 3.95 (d, J=10 Hz), and δ_H 4.20 (m)]. Thus, one of the methyl groups was expected to be modified to a primary alcohol. Since the ^{13}C-NMR data for the ring portion, and C-20 and 21 of **5** were essentially the same as those for **4** (Table 2), one of the germinal methyl groups at C-25 must be oxidized to a carbinol. This was further sup-

ported by the HMBC experiment for **5**, long-range correlations between H-26 (δ_H 3.95) and C-24 (δ_C 217.7), H-27 (δ_H 1.49) and C-24, and C-25 (δ_C 80.0) and C-26 (δ_C 69.2) being observed. The absolute configuration of the newly formed chiral center remains to be determined. Therefore, the structure of tarecilioside L (**5**) was tentatively elucidated to be 26-hydroxytarecilioside K.

Tarecilioside M (**6**), $[\alpha]_D^{25}$ −32.9, was isolated as an amorphous powder and its molecular formula was determined to be $C_{48}H_{78}O_{20}$ on positive-ion HR-ESI-TOF-MS. Tarecilioside M (**6**) was also a cycloartane triglycoside analogous to tarecilioside K (**4**). The difference between the ^{13}C-NMR spectra of **6** and **4** was that one more highly deshielded signal was observed at δ_C 219.9 which was expected to represent one more isolated ketone functional group that was located at C-16, judging from the cross peaks between H_2-15 (δ_H 2.66, 2.72) and H-17 (δ_H 2.35), and C-16 (δ_C 219.9) in the HMBC spectrum. Therefore the structure of tarecilioside M (**6**) was tentatively elucidated to be 16-ketotarecilioside K.

Experimental

General Experimental Procedures IR spectra were obtained on a Horiba Fourier transform infrared spectrophotometer FT-710. Optical rotation data were measured on a JASCO P-1030 polarimeter. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM α-400 spectrometer at 400 MHz and 100 MHz, and a JEOL ECA-600 spectrometer at 600 MHz and 150 MHz, respectively, with tetramethylsilane as an internal standard. Positive-ion HR-ESI-TOF-MS was performed with an Applied Biosystems QSTAR® XL NanoSpray System.

Highly-porous synthetic resin Diaion HP-20 (Φ=60 mm, L=65 cm) was purchased from Mitsubishi Chemical Co., Ltd. (Tokyo, Japan). Silica gel CC was performed on silica gel 60 [E. Merck, Darmstadt, Germany, 70—230 mesh]. Reversed-phase [octadecyl silica gel (ODS)] open CC (RPCC) was performed on Cosmosil 75C_{18}-OPN (Nacalai Tesque, Kyoto, Japan) [Φ=50 mm, L=25 cm, linear gradient: MeOH–H_2O (1 : 9, 1.5 l)→(7 : 3, 1.5 l), 10 g fractions being collected]. DCCC (Tokyo Rikakikai, Tokyo, Japan) was equipped with 500 glass columns (Φ=2 mm, L=40 cm), and the lower and upper layers of a solvent mixture of $CHCl_3$–MeOH–H_2O–1-PrOH (9 : 12 : 8 : 2) were used as the mobile and stationary phases, respectively. Five grams fractions were collected and numbered according to their order of elution with the mobile phase. HPLC was performed on an ODS (Inertsil; GL Science, Tokyo, Japan; Φ=6 mm, L=25 cm, flow rate 1.6 ml/min) column. Precoated silica gel 60 F_{254} TLC plates (E. Merck; 0.25 mm in thickness) were used for identification.

Plant Material Leaves of *T. gracilipes* (Hayata) Ohwi were collected in Okinawa, Japan, in July 2002, and a voucher specimen was deposited in the Herbarium of Pharmaceutical Sciences, Graduate School of Biomedical Sciences, Hiroshima University (02-TG-Okinawa-0705).

Extraction and Isolation The 1-BuOH-soluble fraction (149 g) of a MeOH extract of dried leaves (9.9 kg) of *T. gracilipes*[1] was subjected to highly porous synthetic resin (Diaion HP-20) CC (Φ=60 mm, L=65 cm), using a stepwise-gradient of MeOH–H_2O [(1 : 4, 6 l), (2 : 3, 6 l), (3 : 2, 6 l), (4 : 1, 6 l), and MeOH (6 l)], 500 ml fractions being collected. The residue eluted with the 60—80% MeOH (29.6 g in fractions 14—19) eluate obtained on HP-20 CC was subjected to silica gel (500 g) CC using $CHCl_3$ (3 l), $CHCl_3$–MeOH [(99 : 1, 3 l), (97 : 3, 3 l), (19 : 1, 3 l), (37 : 3, 3 l), (9 : 1, 6 l), (7 : 17, 3 l), (17 : 3, 3 l), (33 : 7, 3 l), (4 : 1, 3 l), (3 : 1, 3 l) (7 : 3, 3 l)] and $CHCl_3$–MeOH–H_2O (35 : 15 : 2, 3 l), fractions of 500 ml being collected. The residue (2.51 g in fractions 59—65) of the 25% MeOH in $CHCl_3$ eluate obtained on silica gel CC was subjected to PRCC. The residue (370 mg in fractions 205—219) was separated by DCCC and then the residue (52.4 mg in fractions 62—72) was separated by HPLC with 65% MeOH to give 7.77 mg of **6** from the peak at 28 min. The residue (480 mg in fractions 220—240) was separated by DCCC to give 323 mg of **4** in fractions 51—66. The residue (302 mg in fractions 241—265) was separated by DCCC. The residue (44.8 mg in fractions 43—53) of the eluate obtained on DCCC was purified by HPLC with 60% MeOH to afford 6.30 mg of **3** from the peak at 6 min, and 14.6 mg of **2** from the peak at 22.4 min. The residue (62.9 mg in fractions 54—74) of the eluate obtained on DCCC was purified by HPLC (Inertsil; GL Science, Tokyo, Japan; Φ=20 mm, L=25 cm, flow rate 4 ml/min) with 70% MeOH to afford 5.83 mg of **5** from the peak at 23.5 min. The residue (65.8 mg in fractions 88—106) of the eluate obtained on DCCC was purified by HPLC with 60% MeOH to afford 21.1 mg of **1** from the peak at 9 min.

Tarecilioside H (**1**): Amorphous powder; $[\alpha]_D^{25}$ −15.5 (c=0.73, pyridine); IR ν_{max} (film) cm^{-1}: 3408, 2971, 1457, 1376, 1368, 1068, 1050; ^{1}H-NMR (400 MHz, pyridine-d_5) and ^{13}C-NMR (100 MHz, pyridine-d_5): Tables 1 and 2, respectively; HR-ESI-MS (positive-ion mode) m/z: 823.4825 $[M+Na]^+$ (Calcd for $C_{42}H_{72}O_{14}Na$: 823.4814).

Tarecilioside I (**2**): Amorphous powder; $[\alpha]_D^{25}$ −10.3 (c=0.77, pyridine); IR ν_{max} (film) cm^{-1}: 3367, 2937, 1592, 1443, 1380, 1070, 1043; ^{1}H-NMR (400 MHz, pyridine-d_5) and ^{13}C-NMR (100 MHz, pyridine-d_5): Tables 1 and 2, respectively; HR-ESI-MS (positive-mode) m/z: 955.5243 $[M+Na]^+$ (Calcd for $C_{47}H_{80}O_{18}Na$: 955.5236).

Tarecilioside J (**3**): Amorphous powder; $[\alpha]_D^{25}$ −18.8 (c=0.22, pyridine); IR ν_{max} (film) cm^{-1}: 3367, 2936, 1704, 1455, 1380, 1074, 1045; ^{1}H-NMR (400 MHz, pyridine-d_5) and ^{13}C-NMR (100 MHz, pyridine-d_5): Tables 1 and 2, respectively; HR-ESI-MS (positive-mode) m/z: 983.5177 $[M+Na]^+$ (Calcd for $C_{48}H_{80}O_{19}Na$: 983.5186).

Tarecilioside K (**4**): Amorphous powder; $[\alpha]_D^{25}$ −5.96 (c=0.75, pyridine); IR ν_{max} (film) cm^{-1}: 3367, 2937, 1701, 1457, 1377, 1075, 1028; ^{1}H-NMR (600 MHz, pyridine-d_5) and ^{13}C-NMR (150 MHz, pyridine-d_5): Tables 1 and 2, respectively; HR-ESI-MS (positive-mode) m/z: 999.5153 $[M+Na]^+$ (Calcd for $C_{48}H_{80}O_{20}Na$: 999.5135).

Tarecilioside L (**5**): Amorphous powder; $[\alpha]_D^{25}$ +1.19 (c=0.17, pyridine); IR ν_{max} (film) cm^{-1}: 3367, 2935, 1702, 1456, 1380, 1074, 1029; ^{1}H-NMR (400 MHz, pyridine-d_5) and ^{13}C-NMR (100 MHz, pyridine-d_5): Tables 1 and 2, respectively; HR-ESI-MS (positive-ion mode) m/z: 999.5141 $[M+Na]^+$ (Calcd for $C_{48}H_{80}O_{20}Na$: 999.5135).

Tarecilioside M (**6**): Amorphous powder; $[\alpha]_D^{25}$ −32.9 (c=0.26, pyridine); IR ν_{max} (film) cm^{-1}: 3376, 2936, 1716, 1457, 1381, 1075, 1028; ^{1}H-NMR (400 MHz, pyridine-d_5) and ^{13}C-NMR (100 MHz, pyridine-d_5): Tables 1 and 2, respectively; HR-ESI-MS (positive-ion mode) m/z: 997.4966 $[M+Na]^+$ (Calcd for $C_{48}H_{78}O_{20}Na$: 997.4978).

Analyses of the Sugar Moiety About 1 mg each of tareciliosides H—M (**1**—**6**) 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_2P-504E, CH_3CN–H_2O (4 : 1), 1 ml/min]. Tareciliosides H (**1**) and J (**3**) gave peaks for L-rhamnose and D-glucose at the retention times of 5.5 min (negative optical rotation sign) and 8.5 min (positive optical rotation sign), respectively, tarecilioside I (**2**) gave peaks for L-rhamnose, D-xylose and D-glucose at the retention times of 5.5 min (negative optical rotation sign), 6.7 min (positive optical rotation sign), and 8.5 min (positive optical rotation sign), respectively, and tareciliosides K (**4**), L (**5**) and M (**6**) each gave a peak for D-glucose at the retention time at 8.5 min (positive optical rotation sign), respectively. Peaks were identified by co-chromatography with anthentic L-rhamnose, D-xylose and D-glucose.

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