Dammarane-Type Triterpene Glycosides from the Leaves of *Rhoiptelea chiliantha*

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Received September 24, 1998; accepted November 17, 1998

In the course of our continuing studies on the chemical constituents of Rhoipteleaceae from the chemotaxonomical point of view, twelve dammarane-type triterpene glycosides, chilianosides A—L, were isolated from the leaves of *Rhoiptelea chiliantha* DIELS *et* Hand.-MAZZ. (Rhoipteleaceae). Their structures were elucidated on the basis of spectral and chemical evidence. Chilianosides B—G possess hydroperoxyl groups in the molecules, whereas chilianosides H—L are the hydroxyl analogues of chilianosides B—G. All of the chilianosides have 20-*R* configurations.

Key words *Rhoiptelea chiliantha*; Rhoipteleaceae; dammarane; triterpene glycoside; chilianoside

In the course of our phytochemical and chemotaxonomical studies on the monotypic family Rhoipteleaceae, a series of novel compounds, *i.e.*, a rearranged-ursane triterpene,[1] triterpene caffeates,[2] triterpene ferulate,[3] triterpene-lignan esters having dimeric structure,[4] diarylheptanoids,[5] dimeric ellagitannins formed by intermolecular oxidative C–C coupling,[6] and euphane-type triterpene bisdesmoside and tridesmosides,[7] have been isolated from *Rhoiptelea chiliantha* DIELS *et* HAND.-MAZZ. Comparison of these metabolites with those of related families, such as Juglandaceae, Betulaceae, Fagaceae and Myricaceae, chemotaxonomically support the viewpoint of the Takhtajan system[8] of plant classification concerning the systematic position of Rhoipteleaceae: this family independently constitutes the order Rhoipteleales which is related to the orders Juglandales (comprising Juglandaceae), Fagales (comprising Betulaceae and Fagaceae) and Myricales (comprising Myricaceae).[5,7] As a part of our continuing research, we describe herein the isolation and structural elucidation of twelve dammarane-type triterpene glycosides from the leaves of this plant.

Results and Discussion

The MeOH extract of the air-dried leaves was suspended in water and sequentially extracted with Et_2O and EtOAc. The EtOAc layer was chromatographed over high porosity polystyrene (MCI-gel CHP 20P) gel, silica gel, Chromatorex octadecyl silica (ODS) gel chromatography and preparative HPLC (ODS) to afford chilianosides A (**1**)—L (**12**).

Chilianoside A (1) Chilianoside A (**1**) was isolated as a white amorphous powder. The ^{13}C-NMR spectrum (Table 1) showed signals derived from a hexose, which was characterized as a β-glucopyranose on the basis of the ^{1}H–^{1}H coupling constants observed in the ^{1}H-NMR spectrum. The remaining 30 carbon signals, namely, eight methyl, eight methylene, eight methine, and six quaternary carbon signals suggested that the aglycone of **1** is a triterpene. The molecular formula of **1** was determined to be $C_{36}H_{62}O_9$ on the basis of its positive FAB-MS (*m/z* 661 for $[M+Na]^+$), ^{13}C-NMR (Table 1) and elemental analysis. In the ^{1}H-NMR spectrum, eight singlet methyls (δ 1.70, 1.64, 1.38×2, 1.17, 1.09, 1.04, 1.03), an olefinic proton (δ 5.31, t, 7 Hz), and three oxygenated methines [δ 3.49 (d, J=9 Hz, H-1), 3.94 (t, J=9 Hz, H-2), 3.37 (d, J=9 Hz, H-3)] were observed. The signals at δ 3.94 were

Table 1. ^{13}C-NMR Spectral Data of Compounds **1**—**7**

No.	**1**[a]	**2**[b]	**3**[c]	**4**[c]	**5**[b]	**5**[d]	**6**[c]	**7**[c]
C-1	84.0	84.5	84.7	84.9	84.5	83.9	84.7	85.0
C-2	72.5	73.0	73.2	73.0	73.0	72.3	73.2	73.0
C-3	92.1	92.5	92.5	93.2	92.6	92.3	92.6	93.2
C-4	40.5	40.8	41.1	41.1	41.0	40.2	41.1	41.1
C-5	53.7	54.3	54.5	54.5	54.3	53.6	54.5	54.5
C-6	18.1	18.8	18.8	18.8	18.8	18.3	18.1	18.8
C-7	35.6	36.2	36.2	36.2	36.2	35.7	36.2	36.3
C-8	41.4	42.2	42.3	42.3	42.3	41.5	42.3	42.3
C-9	52.4	53.2	53.3	53.2	53.3	52.5	53.3	53.3
C-10	43.3	44.2	44.2	44.2	44.2	43.4	44.3	44.2
C-11	24.8	25.2	25.2	25.2	25.2	24.9	25.2	25.2
C-12	28.5	28.7	28.7	28.7	28.8	28.2	28.8	28.8
C-13	42.2	42.9	42.9	42.9	43.1	42.5	43.1	43.1
C-14	50.6	51.2	51.2	51.2	51.2	50.7	51.2	51.2
C-15	31.8	32.2	32.2	32.2	32.2	31.8	32.2	32.2
C-16	25.5	26.1	26.0	26.0	26.0	25.5	25.9	26.0
C-17	50.2	50.96, 50.99	51.0	51.03, 50.78	51.0	50.6	51.0	51.0
C-18	16.1	16.3	16.3	16.3	16.3	14.2	16.4	16.4
C-19	14.5	14.5	14.6	14.6	14.5	14.6	14.5	14.6
C-20	74.3	75.95, 75.91	76.0	75.97, 75.93	76.1	74.8	76.5	76.5
C-21	24.7	23.7	23.7	23.7	23.7	25.1	23.7	23.7
C-22	42.9	38.9	38.9	49.0	46.2	46.2	46.2	46.0
C-23	23.2	26.0	26.0	26.0	127.5	127.1	127.5	127.5
C-24	126.0	91.03, 91.00	91.06, 91.03	91.0	138.3	138.3	138.3	138.4
C-25	130.7	145.9	145.9	145.9	82.6	81.4	82.5	82.6
C-26	25.8	114.1	114.08, 113.99	114.05, 113.97	24.9	25.3	25.0	24.9
C-27	17.8	17.12, 17.09	17.1	17.1	25.0	25.3	25.0	25.0
C-28	28.3	28.5	28.6	28.5	28.5	28.6	28.6	28.5
C-29	17.6	17.5	17.6	17.6	17.5	17.6	17.6	17.6
C-30	16.8	16.9	16.9	16.9	16.8	16.8	16.8	16.8
C-1′	106.4	103.7	106.2	106.3	103.7	103.5	106.2	106.3
C-2′	75.4	75.5	75.4	75.2	75.5	75.6	75.5	75.3
C-3′	78.6	76.1	78.1	77.9	76.5	76.2	78.1	77.9
C-4′	71.6	71.3	71.4	71.6	71.3	72.0	71.4	71.6
C-5′	78.6	78.2	78.1	75.3	78.2	78.9	78.2	75.3
C-6′	62.7	62.2	62.4	64.6	62.3	62.5	62.5	64.6
-Ac		21.3		20.8	21.3	21.4		20.8
		171.6		172.8	171.8	170.1		172.8

a) 125 MHz, C_5D_5N. *b*) 125 MHz, CD_3OD. *c*) 75 MHz, CD_3OD. *d*) 75 MHz, C_5D_5N.

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correlated with both of the other two oxygenated methines in the ^{1}H–^{1}H correlated spectroscopy (COSY) spectrum. Further detailed analyses of one-dimensional (1D) and two-dimensional (2D)-NMR spectra of **1** permitted us to determine the gross structure of its aglycone: a combination of a ^{1}H-detected heteronuclear single quantum coherence (HSQC) experiment and a ^{1}H–^{1}H COSY spectral analysis allowed us to identify four isolated spin systems of the aglycone moiety (heavy lines shown in Fig. 1). Furthermore, the ^{1}H-detected heteronuclear multiple bond correlations (HMBC) shown in Fig. 1 determined the connectivity of these spin systems as well as the location of the glucose at the C-3 position of the aglycone. The large $J_{H1,H2}$ and $J_{H2,H3}$ values (9 Hz) indicated an *axial* orientation of these protons. The remaining relative configuration of **1** was determined by nuclear Overhauser enhancement spectroscopy (NOESY) correlations as shown in Fig. 2, which unambiguously revealed that the aglycone is a dammarane-type triterpene. Finally, the C-20 configuration of **1** was established to be *R* on the basis of comparison of the ^{13}C-NMR chemical shifts of C-20, 21, 22 (Fig. 3) with those of dammarenediol I (20*R*) and dammarenediol II (20*S*).[9] Consequently, the structure of chilianoside A was assigned as the formula **1**.

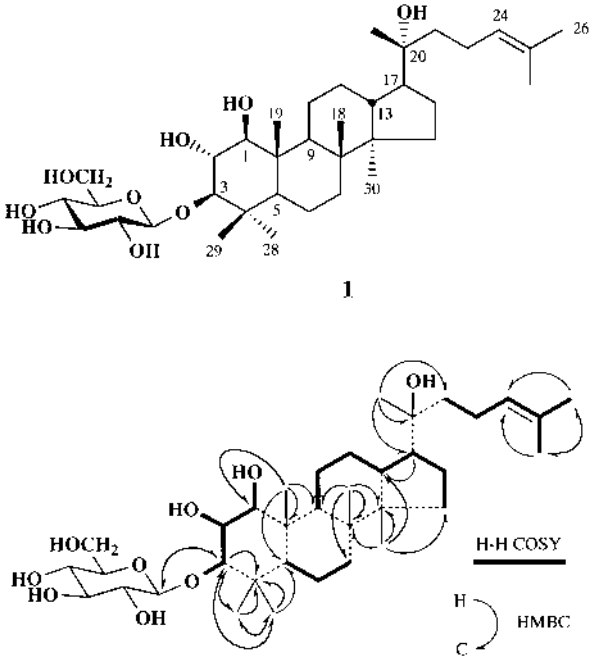


Fig. 1. Partial Structures and HMBC Correlations of **1**

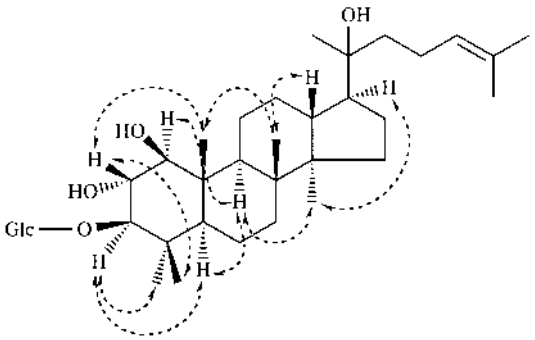


Fig. 2. NOE Correlations of the Aglycone of **1**

Chilianoside B (2) Chilianoside B was isolated as a white amorphous powder. The ^{1}H-NMR spectrum of **2** displayed signals assignable to 2-*O*-acetylglucopyranose [4.80 (d, J=8, 9 Hz, glc-2), 4.53 (d, J=8 Hz, glc-1), 3.89 (dd, J=2, 12 Hz, glc-6a), 3.68 (dd, J=6, 12 Hz, glc-6b), 3.52 (t, J=9 Hz, glc-3), 3.40 (t, J=9 Hz, glc-4), 3.36 (m, glc-5), 2.09 (s, acetyl)], and the signals derived from a triterpene moiety which are closely related to those of **1**. In the ^{13}C-NMR spectrum (Table 1), 22 of the 30 carbon signals due to the triterpene moiety were in good agreement with those of the A—D rings of **1**, suggesting that the aglycone of **2** is also a dammarane-type triterpene. As for the side chain parts, analysis of the ^{1}H–^{1}H COSY and HMBC spectrum (Fig. 4) established the carbon connectivity from C-20 to C-27 of **2**. Comparison of the chemical shifts of H-24 (δ 4.16) and C-24 (δ 91.0) of **2** with those of a triterpene having the same side chain structure[10] suggested the presence of a hydroperoxyl group at C-24. This was supported by the $[M+Na]^+$ peak at *m/z* 735 in the positive FAB-MS spectrum, and by its positive reaction to KI-starch test. Compound **2** was found to be an inseparable mixture of 24*R* and 24*S* epimers based on the fact that the signals of C-17, 20, 24, 27 appeared in pairs in the ^{13}C-NMR spectrum (Table 1). On the basis of above evi-

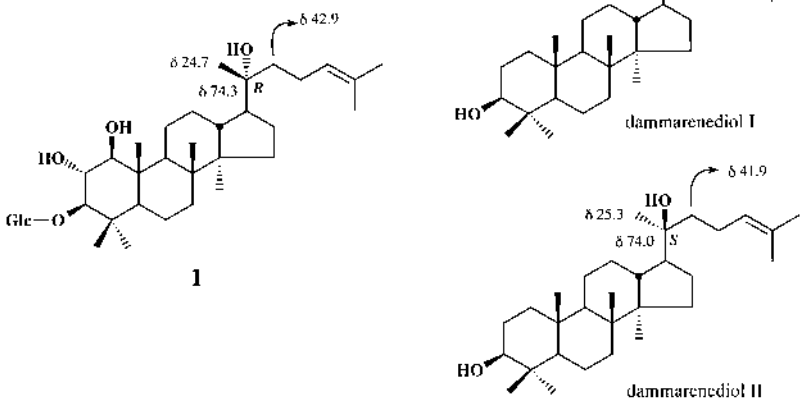


Fig. 3. Comparison of Chemical Shifts of C-20, 21, 22 of **1** with Those of Related Compounds

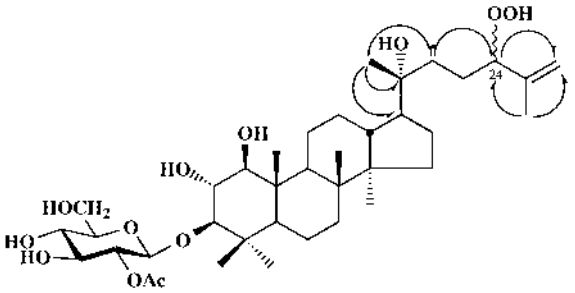


Fig. 4. Selected HMBC Correlations (H to C) of **2**

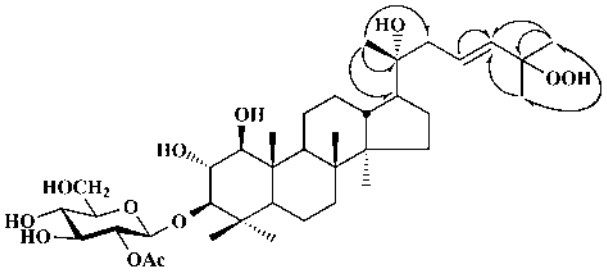
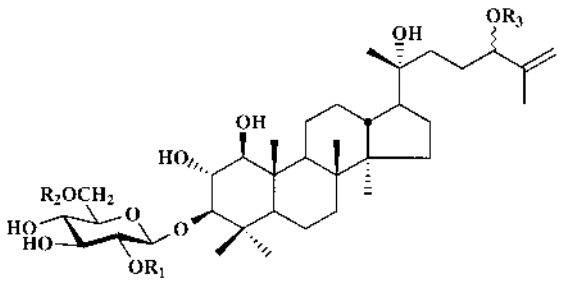
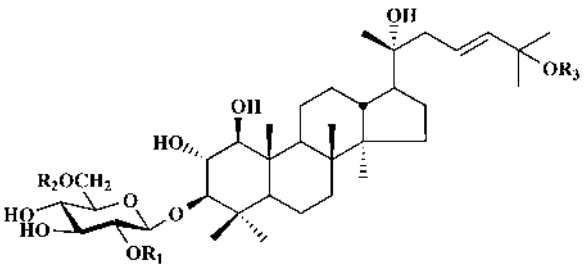


Fig. 5. Selected HMBC Correlations (H to C) of **5**



	R_1	R_2	R_3
2:	Ac	H	OH
3:	H	H	OH
4:	H	Ac	OH
8:	H	H	H
9:	Ac	H	H
10:	H	Ac	H



	R_1	R_2	R_3
5:	Ac	H	OH
6:	H	H	OH
7:	H	Ac	OH
11:	H	H	H
12:	H	Ac	H

dence, the structure of chilianoside B was characterized as formula **2**.

Chilianosides C (3) and D (4) Both chilianosides C (**3**) and D (**4**) were also positive to KI-starch test, suggesting the presence of hydroperoxyl groups in the molecules. Their ^{1}H- and ^{13}C-NMR spectra are quite similar to those of **2** except for the sugar part, indicating that the aglycone of **3** and **4** was the same as that of **2**. In the ^{1}H-NMR of **3**, signals derived from an acetyl group were not observed, and H-2 of glucose was shifted upfield by 1.50 ppm compared with that of **2**. Taking the $[M-H]^-$ ion peak at *m/z* 669 in the negative FAB-MS into account, **3** was determined to be a deacetyl derivative of **2**.

Compound **4** exhibited an $[M-H]^-$ ion peak at *m/z* 711 in the negative FAB-MS, indicating that the molecular weight of **4** is the same as that of **2**. The ^{1}H- and ^{13}C-NMR spectra showed the presence of an acetyl group in the molecule. However, H_2-6 and H-2 of the glucosyl group were found to be shifted to lower field by 0.55, 0.49 ppm, and upper field by 1.50 ppm, respectively, compared with those of **2**. These facts revealed that the sugar moiety of **4** is a 6-*O*-acetylglucopyranose. From these results, the structure of chilianoside D was concluded to be as shown by the formula **4**. The duplicate carbon signals of the side chain parts of **3** and **4** implied that these compounds are a mixture of C-24 epimers.

Chilianoside E (5) Chilianoside E (**5**) was isolated as a white amorphous powder which has the same molecular formula as **2** on the basis of the $[M+Na]^+$ peak at *m/z* 735 in the positive FAB-MS and ^{13}C-NMR spectral data. The ^{1}H- and ^{13}C-NMR spectra of **5** closely resembled those of **2**, especially the signals arising from the sugar moiety and the rings A—D, indicating that **5** is also a hydroperoxydammarane glycoside which differed with **2** only in the structure of side chain part. Detailed analysis of the ^{1}H–^{1}H COSY and HMBC spectrum (Fig. 5) finally disclosed the structure of the side chain with a hydroperoxyl group at C-25, which was supported by the chemical shift comparison with those of related hydroperoxylated triterpenes.[11,12] Thus, the structure of **5** was assigned to chilianoside E.

Chilianosides F (6) and G (7) Chilianosides F (**6**) and G (**7**) showed an $[M-H]^-$ ion peak at *m/z* 669 and 711, respectively, in their negative FAB-MS. In a similar manner described for **3** and **4**, **6** was concluded to be a deacetyl derivative of **5**, and **7** to be 6′-*O*-acetyl isomer of **6**, respectively, based on the interpretation of their ^{1}H- and ^{13}C-NMR spectral data.

The structures of chilianosides C (**3**) and F (**6**) suggested that they are generated by sensitized photooxygenation[13] of chilianoside A (**1**) in which singlet oxygen ($^1O_2$) was involved. Actually, photooxygenation of **1** in MeOH using Rose Bengal as a sensitizer yielded **3** and **6** as expected. This result further supplied additional evidence for the structures of **3** and **6**. Since singlet oxygen is known to be present in plant tissue,[14] it is probable that these hydroperoxylated triterpene glycosides are generated in the plant.

Chilianosides H (8), I (9), and J (10) Chilianoside H (**8**) displayed an $[M-H]^-$ ion peak at *m/z* 677 $(M+Na)^+$ in the positive FAB-MS, corresponding to a molecular formula of $C_{36}H_{62}O_{10}$ which is one oxygen atom less than 3. The ^{1}H- and ^{13}C-NMR data (Table 2) of **8** are in good agreement with those of **3**, except for the upfield shifts of H-24 by 0.21 ppm and C-24 by 13.6 ppm. This observation suggested that the hydroperoxyl group at C-24 of **3** is replaced by a hydroxyl group in **8**, and this was verified by the reduction of **3** with triphenylphosphine to afford **8**.

Compounds **9** and **10** were deduced to be 2′-*O*-acetyl and

6′-*O*-acetyl derivatives of **8**, respectively, on the basis of their FAB-MS, ^{1}H- and ^{13}C-NMR data (Table 2) which were closely related to those of **3** and **4**. The structures of **9** and **10** were confirmed by acetylation yielding the same hexaacetate whose spectral data were identical with those of the acetate (**8a**) of **8** (Chart 1). Furthermore, compounds **8**, **9** and **10** were all judged to be mixtures of 24-epimers from the appearance of the carbon signals of the side chain parts in duplicate.

Table 2. ^{13}C-NMR Spectral Data of Compounds **8**—**12**

No.	**8**[a]	**8**[b]	**9**[b]	**10**[a]	**11**[a]	**12**[a]
C-1	84.7	84.1	83.9	84.9	84.7	85.0
C-2	73.2	72.3	72.3	73.0	73.2	73.0
C-3	92.6	92.1	92.3	93.2	92.6	93.2
C-4	41.1	40.5	40.4	41.1	41.1	41.1
C-5	54.5	53.7	53.6	54.5	54.5	54.5
C-6	18.8	18.1	18.2	18.8	18.1	18.8
C-7	36.2	35.7	35.7	36.3	36.3	36.2
C-8	42.3	41.5	41.5	42.3	42.3	42.3
C-9	53.3	52.5	52.5	53.3	53.3	53.3
C-10	44.3	43.4	43.4	44.2	44.3	44.2
C-11	25.2	24.9	24.9	25.2	25.2	25.2
C-12	28.8	28.5	28.6	28.8	28.8	28.8
C-13	43.0	42.3	42.4	43.0	43.1	43.1
C-14	51.2	50.6	50.7	51.2	51.2	51.2
C-15	32.2	31.8	31.9	32.2	32.2	32.2
C-16	26.1	25.7	25.7	26.1	26.0	26.0
C-17	51.3, 51.1	50.5, 50.4	50.55, 50.48	51.1	50.9	50.9
C-18	16.3	16.1	16.2	16.3	16.4	16.3
C-19	14.6	14.6	14.6	14.5	14.5	14.6
C-20	76.1, 76.0	74.4	74.5	76.0	76.5	76.5
C-21	23.8, 23.7	24.9	25.09, 25.04	23.9, 23.7	23.8	23.7
C-22	39.0	39.3, 39.2	39.40, 39.32	38.9	45.9	46.0
C-23	29.9	30.5, 30.4	30.61, 30.51	30.0	123.8	123.9
C-24	77.4	76.3, 76.2	76.27, 76.20	77.4	142.1	142.1
C-25	148.9	149.9	149.6	148.9	71.2	71.2
C-26	111.5, 111.4	110.3, 110.1	110.4, 110.2	111.37, 111.30	29.9	29.9
C-27	17.7, 17.6	18.3, 18.2	18.37, 18.27	17.7	30.0	30.0
C-28	28.6	28.4	28.3	28.5	28.6	28.5
C-29	17.6	17.7	17.6	17.6	17.6	17.6
C-30	16.9	16.8	16.9	16.9	16.8	16.8
C-1′	106.2	106.5	103.5	106.3	106.2	106.3
C-2′	75.5	75.5	75.6	75.3	75.5	75.2
C-3′	78.1	78.7	75.4	77.9	78.1	77.9
C-4′	71.4	71.7	72.0	71.6	71.4	71.6
C-5′	78.1	78.7	78.9	75.3	78.2	75.3
C-6′	62.5	62.7	62.5	64.6	62.5	64.6
-Ac			21.4	20.8		20.8
			170.1	172.8		172.8

a) 75 MHz, CD_3OD. *b*) 75 MHz, C_5D_5N.

Chilianosides K (11) and L (12) Chilianoside K (**11**) was suggested to be a C-25 hydroxyl analogue of **6** on the basis of comparison of its negative FAB-MS (*m/z* 653 for $[M-H]^-$), ^{1}H- and ^{13}C-NMR data (Table 2) with those of **6**. This was also confirmed by the reduction of **6** with triphenylphosphine to afford **11**. Chilianoside L (**12**) exhibited an $[M-H]^-$ ion peak at *m/z* 695 in the negative FAB-MS which is 42 mass units more than that of **11**. The signals arising from the aglycone of **12** were almost identical with those of **11**. However, signals due to an acetyl group appeared in the ^{1}H- and ^{13}C-NMR spectra, along with a downfield shift by 0.55, 0.51 ppm of the H_2-6′ signals. These results let us conclude 12 to be a 6′-*O*-acetyl derivative of **11**.

Conclusion

We have isolated twelve glycosides with a new 1,2,3-trihydroxylated dammarane-type triterpene as the aglycone from the air-dried leaves of *Rhoiptelea chiliantha*. Among them, chilianosides B (**2**)—G (**7**) have a hydroperoxyl group in the molecules, and chilianosides H (**8**)—L (**12**) are their hydroxyl analogues. Although hydroperoxydammarane triterpenes have been isolated from *Gymnema sylvestre* (Asclepidaceae)[11] and *Panax notoginseng* (Araliaceae),[12] chilianosides B (**2**)—G (**7**) are the first report of hydroperoxydammarane triterpene glycoside with a 20*R* configuration. On the other hand, since a considerable number of dammarane triterpenes have been isolated from *Betula plants*,[15] the chilianosides may be additional chemical evidence to explain the relationships between Rhoipteleaceae and Betulaceae.

Experimental

General The instruments used to measure the physical data and the experimental conditions for chromatography were the same as those described in our previous paper.[3]

Plant Material The leaves of *Rhoiptelea chiliantha* were collected in Guangxi, China in October, 1988. A voucher specimen has been deposited in the Laboratory of Plant Chemotaxonomy, China Pharmaceutical University, Nanjing, China.

Extraction and Separation The MeOH extract of the air-dried leaves (510 g) was suspended in H_2O, and sequentially extracted with Et_2O and EtOAc. The EtOAc layer (31.0 g) was chromatographed over MCI-gel CHP 20P (0—100% MeOH). The eluates (13.2 g) from 40—70% MeOH were further chromatographed over silica gel [$CHCl_3$–MeOH–H_2O (9 : 1 : 0.1—7 : 3 : 0.5)] to afford fraction-1 (2.2 g), fraction-2 (0.96 g), chilianoside A (**1**) (297 mg) and fraction-3 (5.6 g). Fraction-1 was applied to a column of Chromatorex ODS (80—100% MeOH) and finally purified by preparative HPLC (ODS, 90% MeOH, detector: RI) to give chilianosides D (**4**, 19 mg), G (**7**, 10 mg), J (**10**, 21 mg) and L (**12**, 14 mg). In the same isolation precedure as

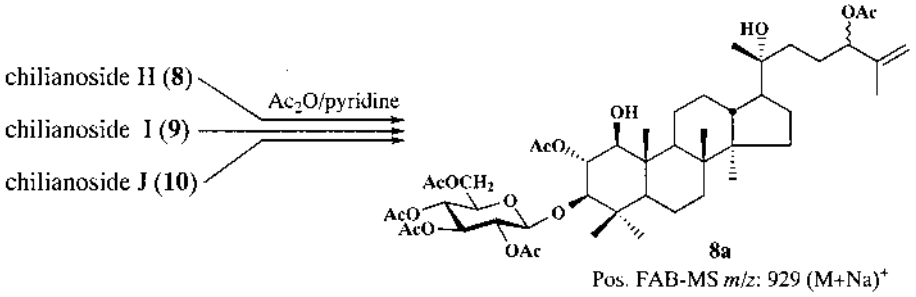


Chart 1

described for fraction-1, chilianosides B (**2**, 22 mg), E (**5**, 22 mg) and I (**9**, 11 mg) were obtained from fraction-2, chilianosides C (**3**, 33 mg), F (**6**, 52 mg), H (**8**, 25 mg) and K (**11**, 6 mg) were obtained from fraction-3.

Chilianoside A (**1**): A white amorphous powder, $[\alpha]_D^{20}$ +5.5° (c=0.3, pyridine). *Anal.* Calcd for $C_{36}H_{62}O_9 \cdot 3/4H_2O$: C, 66.28; H, 9.81. Found: C, 66.22; H, 9.52. Positive FAB-MS *m/z*: 661 $(M+Na)^+$. ^{1}H-NMR (500 MHz, CD_3OD): δ 5.31 (1H, t, J=7 Hz, H-24), 4.96 (1H, d, J=8 Hz, glc-1), 4.64 (1H, dd, J=2, 12 Hz, glc-6a), 4.33 (1H, dd, J=6, 12 Hz, glc-6b), 4.25 (1H, dd, J=8, 9 Hz, glc-3), 4.16 (1H, t, J=9 Hz, glc-4), 4.12 (1H, m, glc-5), 4.07 (1H, t, J=8 Hz, glc-2), 3.94 (1H, t, J=9 Hz, H-2), 3.49 (1H, d, J=9 Hz, H-1), 3.37 (1H, d, J=9 Hz, H-3), 3.04 (1H, dd, J=3, 15 Hz, H-11a), 2.52, 2.34 (each 1H, m, H_2-23), 2.32, 1.53 (each 1H, m, H_2-12), 2.05 (1H, m, H-13), 1.99 (1H, m, H-17), 1.86, 1.74 (each 1H, m, H_2-16), 1.78, 1.76 (each 1H, m, H_2-22), 1.73 (1H, m, H-9), 1.70 (3H, s, H_3-26), 1.64 (3H, s, H_3-27), 1.62, 1.55 (each 1H, m, H_2-6), 1.62 (1H, m, H-15b), 1.60 (1H, m, H-11b), 1.55, 1.27 (each 1H, m, H_2-7), 1.38 (6H, s, H_3-21, 28), 1.17 (3H, s, H_3-19), 1.14 (1H, d, J=12 Hz, H-15a), 1.07 (3H, s, H_3-29), 1.04 (3H, s, H_3-18), 1.03 (3H, s, H_3-30), 0.89 (1H, m, H-5). ^{13}C-NMR data see Table 1.

Chilianoside B (**2**): A white amorphous powder, $[\alpha]_D^{20}$ +29.4° (c=0.2, MeOH). *Anal.* Calcd for $C_{38}H_{64}O_{12} \cdot H_2O$: C, 62.44; H, 9.10. Found: C, 62.22; H, 8.77. Positive FAB-MS *m/z*: 735 $(M+Na)^+$. ^{1}H-NMR (500 MHz, CD_3OD): δ 4.92 (1H, dd, J=2, 3 Hz, H-26b), 4.91 (1H, s, H-26a), 4.80 (1H, d, J=8, 9 Hz, glc-2), 4.53 (1H, d, J=8 Hz, glc-1), 4.16 (1H, t, J=6 Hz, H-24), 3.89 (1H, dd, J=2, 12 Hz, glc-6a), 3.68 (1H, dd, J=6, 12 Hz, glc-6b), 3.52 (1H, t, J=9 Hz, glc-3), 3.46 (1H, t, J=9 Hz, H-2), 3.40 (1H, t, J=9 Hz, glc-4), 3.36 (1H, m, glc-5), 3.13 (1H, d, J=9 Hz, H-1), 3.04 (1H, d, J=9 Hz, H-3), 2.48 (1H, dd, J=13 Hz, H-11a), 2.09 (3H, s, acetyl), 1.90, 1.28 (each 1H, m, H_2-12), 1.71 (3H, s, H_3-27), 1.70 (1H, m, H-13), 1.67 (1H, m, H-17), 1.66, 1.35 (each 1H, m, H_2-16), 1.63, 1.50 (each 1H, m, H_2-23), 1.60, 1.26 (each 1H, m, H_2-6), 1.58, 1.26 (each 1H, m, H_2-7), 1.54 (1H, m, H-9), 1.50, 1.36 (each 1H, m, H_2-22), 1.36 (1H, m, H-11b), 1.47, 1.03 (1H, m, H_2-15), 1.07 (3H, s, H_3-21), 0.99 (3H, s, H_3-18), 0.98 (3H, s, H_3-28), 0.96 (3H, s, H_3-19), 0.90 (3H, s, H_3-30), 0.81 (1H, m, H-5), 0.76 (3H, s, H_3-29). ^{13}C-NMR data see Table 1.

Chilianoside C (**3**): A white amorphous powder, $[\alpha]_D^{15}$ +13.7° (c=0.2, MeOH). *Anal.* Calcd for $C_{36}H_{62}O_{11} \cdot 3/2H_2O$: C, 61.96; H, 9.39. Found: C, 61.53; H, 8.99. Negative FAB-MS *m/z*: 669 $(M-H)^-$. ^{1}H-NMR (300 MHz, CD_3OD): δ 5.00, 4.79 (each 1H, s, H_2-26), 4.34 (1H, d, J=8 Hz, glc-1), 4.16 (1H, t, J=6 Hz, H-24), 3.88 (1H, d, J=12 Hz, glc-6a), 3.66 (1H, dd, J=5, 12 Hz, glc-6b), 3.50 (1H, t, J=9 Hz, H-2), 3.16 (1H, d, J=9 Hz, H-1), 3.05 (1H, d, J=9 Hz, H-3), 1.71 (3H, s, H_3-27), 1.08×2, 0.99, 0.98, 0.90, 0.89 (each 3H, s, H_3-18, 19, 21, 28, 29, 30). ^{13}C-NMR data see Table 1.

Chilianoside D (**4**): A white amorphous powder, $[\alpha]_D^{15}$ +15.5° (c=0.2, MeOH). *Anal.* Calcd for $C_{38}H_{64}O_{12} \cdot 3/4H_2O$: C, 62.83; H, 9.09. Found: C, 62.48; H, 8.57. Negative FAB-MS *m/z*: 711 $(M-H)^-$. ^{1}H-NMR (300 MHz, CD_3OD): δ 4.91, 4.78 (each 1H, s, H_2-26), 4.44 (1H, d, J=12 Hz, glc-6a), 4.34 (1H, d, J=8 Hz, glc-1), 4.17 (1H, dd, J=5, 12 Hz, glc-6b), 4.16 (1H, t, J=6 Hz, H-24), 3.50 (1H, t, J= 9 Hz, H-2), 3.16 (1H, d, J=9 Hz, H-1), 3.05 (1H, d, J=9 Hz, H-3), 2.09 (3H, s, acetyl), 1.71 (3H, s, H_3-27), 1.08×2, 0.99, 0.98, 0.90, 0.89 (each 3H, s, H_3-18, 19, 21, 28, 29, 30). ^{13}C-NMR data see Table 1.

Chilianoside E (**5**): A white amorphous powder, $[\alpha]_D^{20}$ +44.0° (c=0.2, MeOH). *Anal.* Calcd for $C_{38}H_{64}O_{12} \cdot 5/4H_2O$: C, 62.06; H, 9.11. Found: C, 61.76; H, 8.65. Positive FAB-MS *m/z*: 735 $(M+Na)^+$. ^{1}H-NMR (500 MHz, CD_3OD): δ 5.75 (1H, dt, J=16, 7 Hz, H-23), 5.59 (1H, d, J=16 Hz, H-24), 4.53 (1H, d, J=8 Hz, glc-1), 4.80 (1H, d, J=8, 9 Hz, glc-2), 3.89 (1H, dd, J=2, 12 Hz, glc-6a), 3.68 (1H, dd, J=6, 12 Hz, glc-6b), 3.52 (1H, t, J=9 Hz, glc-3), 3.46 (1H, t, J=9 Hz, H-2), 3.40 (1H, t, J=9 Hz, glc-4), 3.35 (1H, m, glc-5), 3.14 (1H, d, J=9 Hz, H-1), 3.04 (1H, d, J=9 Hz, H-3), 2.48 (1H, dd, J=13 Hz, H-11a), 2.18 (2H, m, H_2-22), 2.09 (3H, s, acetyl), 1.91 (1H, d, J=13 Hz, H-12a), 1.72 (1H, m, H-13), 1.69 (1H, m, H-17), 1.68, 1.36 (each 1H, m, H_2-16), 1.59, 1.27 (each 1H, m, H_2-6), 1.58, 1.25 (each 1H, m, H_2-7), 1.56 (1H, m, H-9), 1.49, 1.05 (1H, m, H_2-15), 1.36 (1H, m, H-11b), 1.30 (6H, s, H_3-26, 27), 1.26 (1H, m, H-12b), 1.08 (3H, s, H_3-21), 1.00 (3H, s, H_3-18), 0.98 (3H, s, H_3-28), 0.97 (3H, s, H_3-19), 0.89 (3H, s, H_3-30), 0.81 (1H, m, H-5), 0.76 (3H, s, H_3-29). ^{13}C-NMR data see Table 1.

Chilianoside F (**6**): A white amorphous powder, $[\alpha]_D^{15}$ +11.1° (c=0.2, MeOH). *Anal.* Calcd for $C_{36}H_{62}O_{11} \cdot 3/2H_2O$: C, 61.96; H, 9.39. Found: C, 61.92; H, 9.02. Negative FAB-MS *m/z*: 669 $(M-H)^-$. ^{1}H-NMR (300 MHz, CD_3OD): δ 5.76 (1H, dt, J=16, 7 Hz, H-23), 5.59 (1H, d, J= 16 Hz, H-24), 4.33 (1H, d, J=8 Hz, glc-1), 3.88 (1H, dd, J=2, 12 Hz, glc-6a), 3.66 (1H, dd, J=5, 12 Hz, glc-6b), 3.50 (1H, t, J= 9 Hz, H-2), 3.16 (1H, d, J=9 Hz, H-1), 3.05 (1H, d, J=9 Hz, H-3), 1.29 (6H, s, H_3-26, 27), 1.08×2, 1.00, 0.98, 0.89, 0.89 (each 3H, s, H_3-18, 19, 21, 28, 29, 30). ^{13}C-NMR data see Table 1.

Chilianoside G (**7**): A white amorphous powder, $[\alpha]_D^{15}$ +13.6° (c=0.2, MeOH). *Anal.* Calcd for $C_{38}H_{64}O_{12} \cdot 3/4H_2O$: C, 62.83; H, 9.09. Found: C, 62.66; H, 8.79. Negative FAB-MS *m/z*: 711 $(M-H)^-$. ^{1}H-NMR (300 MHz, CD_3OD): δ 5.76 (1H, dt, J=16, 7 Hz, H-23), 5.59 (1H, d, J=16 Hz, H-24), 4.43 (1H, dd, J=2, 12 Hz, glc-6a), 4.34 (1H, d, J=8 Hz, glc-1), 4.17 (1H, dd, J=6, 12 Hz, glc-6b), 3.48 (1H, t, J=9 Hz, H-2), 3.15 (1H, d, J=9 Hz, H-1), 3.02 (1H, d, J=9 Hz, H-3), 2.09 (3H, s, acetyl), 1.27 (6H, s, H_3-26, 27), 1.08×2, 1.00, 0.98, 0.89×2 (each 3H, s, H_3-18, 19, 21, 28, 29, 30). ^{13}C-NMR data see Table 1.

Chilianoside H (**8**): A white amorphous powder, $[\alpha]_D^{15}$ +13.0° (c=1, MeOH). *Anal.* Calcd for $C_{36}H_{62}O_{10} \cdot 1/4H_2O$: C, 65.58; H, 9.55. Found: C, 65.55; H, 9.17. Positive FAB-MS *m/z*: 677 $(M+Na)^+$. ^{1}H-NMR (300 MHz, CD_3OD): δ 4.88, 4.80 (each 1H, s, H2-26), 4.33 (1H, d, J=8 Hz, glc-1), 3.95 (1H, t, J=6 Hz, H-24), 3.88 (1H, d, J=12 Hz, glc-6a), 3.66 (1H, dd, J=5, 12 Hz, glc-6b), 3.50 (1H, t, J=9 Hz, H-2), 3.16 (1H, d, J=9 Hz, H-1), 3.05 (1H, d, J=9 Hz, H-3), 1.71 (3H, s, H_3-27), 1.08×2, 1.00, 0.98, 0.91, 0.89 (each 3H, s, H_3-18, 19, 21, 28, 29, 30). ^{1}H-NMR (300 MHz, C_5D_5N): δ 5.28, 5.25 (each 1H, s, H_2-26), 4.98 (1H, d, J=8 Hz, glc-1), 4.66 (1H, d, J=11 Hz, glc-6a), 4.43 (1H, t, J=6 Hz, H-24), 4.34 (1H, dd, J=6, 11 Hz, glc-6b), 4.27 (1H, dd, J=8, 9 Hz, glc-3), 4.18 (2H, m, glc-4, 5), 4.09 (1H, t, J=8 Hz, glc-2), 3.85 (1H, t, J= 9 Hz, H-2), 3.49 (1H, d, J=9 Hz, H-1), 3.38 (1H, d, J=9 Hz, H-3), 1.92 (3H, s, H_3-27), 1.40, 1.39, 1.17, 1.08, 1.04, 1.00 (each 3H, s, H_3-18, 19, 21, 28, 29, 30). ^{13}C-NMR data see Table 2.

Chilianoside I (**9**): A white amorphous powder, $[\alpha]_D^{15}$ +22.0° (c=0.2, MeOH). *Anal.* Calcd for $C_{38}H_{64}O_{11} \cdot 5/4H_2O$: C, 63.44; H, 9.32. Found: C, 63.38; H, 9.03. Positive FAB-MS *m/z*: 719 $(M+Na)^+$. ^{1}H-NMR (300 MHz, C_5D_5N): δ 5.63 (1H, t, J=8 Hz, glc-2), 5.27, 5.25 (each 1H, s, H_2-26), 5.02 (1H, d, J=8 Hz, glc-1), 4.63 (1H, d, J=11 Hz, glc-6a), 4.43 (1H, t, J=6 Hz, H-24), 3.85 (1H, t, J=9 Hz, H-2), 3.45 (1H, d, J=9 Hz, H-1), 3.27 (1H, d, J=9 Hz, H-3), 1.92 (3H, s, H_3-27), 2.17 (3H, s, acetyl), 1.40, 1.12, 1.11, 1.02, 0.99, 0.97 (each 3H, s, H_3-18, 19, 21, 28, 29, 30). ^{13}C-NMR data see Table 2.

Chilianoside J (**10**): A white amorphous powder, $[\alpha]_D^{15}$ +16.7° (c=0.2, MeOH). *Anal.* Calcd for $C_{38}H_{64}O_{11} \cdot 4/3H_2O$: C, 64.25; H, 9.29. Found: C, 64.02; H, 9.05. Negative FAB-MS *m/z*: 695 $(M-H)^-$. ^{1}H-NMR (300 MHz, CD_3OD): δ 4.89, 4.79 (each 1H, s, H_2-26), 4.43 (1H, dd, J=2, 12 Hz, glc-6a), 4.34 (1H, d, J=8 Hz, glc-1), 4.17 (1H, dd, J=6, 12 Hz, glc-6b), 3.94 (1H, t, J=6 Hz, H-24), 3.48 (1H, t, J=9 Hz, H-2), 3.14 (1H, d, J=9 Hz, H-1), 3.02 (1H, d, J=9 Hz, H-3), 2.09 (3H, s, acetyl), 1.71 (3H, s, H_3-27), 1.09, 1.08, 1.00, 0.98, 0.91, 0.89 (each 3H, s, H_3-18, 19, 21, 28, 29, 30). ^{13}C-NMR data see Table 2.

Chilianoside K (**11**): A white amorphous powder, $[\alpha]_D^{15}$ +10.3° (c=0.2, MeOH). *Anal.* Calcd for $C_{36}H_{62}O_{10} \cdot 3/2H_2O$: C, 63.41; H, 9.6. Found: C, 63.39; H, 9.16. Negative FAB-MS *m/z*: 653 $(M-H)^-$. ^{1}H-NMR (300 MHz, CD_3OD): δ 5.71 (1H, dt, J=16, 7 Hz, H-23), 5.59 (1H, d, J=16 Hz, H-24), 4.33 (1H, d, J=8 Hz, glc-1), 3.88 (1H, dd, J=2, 12 Hz, glc-6a), 3.66 (1H, dd, J=5, 12 Hz, glc-6b), 3.51 (1H, t, J=9 Hz, H-2), 3.16 (1H, d, J=9 Hz, H-1), 3.05 (1H, d, J=9 Hz, H-3), 1.27 (6H, s, H_3-26, 27), 1.08×2, 1.00, 0.98, 0.90, 0.89 (each 3H, s, H_3-18, 19, 21, 28, 29, 30). ^{13}C-NMR data see Table 2.

Chilianoside L (**12**): A white amorphous powder, $[\alpha]_D^{15}$ +14.2° (c=0.2, MeOH). *Anal.* Calcd for $C_{38}H_{64}O_{11} \cdot 5/4H_2O$: C, 63.44; H, 9.32. Found: C, 63.17; H, 8.88. Negative FAB-MS *m/z*: 695 $(M-H)^-$. ^{1}H-NMR (300 MHz, CD_3OD): δ 5.71 (1H, dt, J=16, 7 Hz, H-23), 5.60 (1H, d, J=16 Hz, H-24), 4.43 (1H, dd, J=2, 12 Hz, glc-6a), 4.33 (1H, d, J=8 Hz, glc-1), 4.17 (1H, dd, J=6, 12 Hz, glc-6b), 3.48 (1H, t, J= 9 Hz, H-2), 3.14 (1H, d, J=9 Hz, H-1), 3.02 (1H, d, J=9 Hz, H-3), 2.09 (3H, s, acetyl), 1.27 (6H, s, H_3-26, 27), 1.08 ×2, 1.00, 0.98, 0.90, 0.89 (each 3H, s, H_3-18, 19, 21, 28, 29, 30). ^{13}C-NMR data see Table 2.

Acetylation of 8, 9, and 10 **8** (10 mg) was treated with Ac_2O (0.5 ml) and pyridine (0.5 ml) and left to stand at room temperature overnight affording **8a** (9 mg): a white amorphous powder, $[\alpha]_D^{15}$ −8.2° (c=0.7, MeOH). Positive FAB-MS *m/z*: 929 $(M+Na)^+$. ^{1}H-NMR (500 MHz, CD_3OD): δ 5.21 (1H, t, J=10 Hz, glc-3), 5.10 (1H, t, J=6 Hz, H-24), 5.10 (2H, t, J=10 Hz, H-2, glc-4), 4.91, 4.90 (each 1H, d, J=1 Hz, H_2-27), 4.85 (1H, dd, J=8, 10 Hz, glc-2), 4.74 (1H, d, J=8 Hz, glc-1), 4.41 (1H, dd, J=4, 13 Hz, glc-6), 4.04 (1H, dd, J=2, 13 Hz, glc-6), 3.85 (1H, ddd, J=2, 4, 10 Hz, glc-5), 3.28, 3.27 (each 1H, d, J=10 Hz, H-1, 3), 2.08, 2.05, 2.04, 2.01, 1.99, 1.95 (each 3H, s, acetyl), 1.72 (3H, s, H_3-26), 1.08, 1.05, 1.02, 1.00, 0.91, 0.82 (each 3H, s, H_3-18, 19, 21, 28, 29, 30).

9 (2 mg) and **10** (2 mg) were acetylated separately in a manner similar to that described for **8** to furnish acetylated products (1.5 mg and 1.5 mg, respectively), which were identified to be the same as the acetylated product of **8** by comparing their positive FAB-MS and ^{1}H-NMR spectral data with

those of **8a**.

Photosensitized Oxygenation of 1 A solution of **1** (160 mg) and Rose Bengal (15 mg) in MeOH (20 ml) was stirrred and irridated with a 400W lamp under an oxygen atomosphere at room temperature for 10 h. After filtration, the filtrate was concentrated and separated by silica gel chromatography [$CHCl_3$–MeOH–H_2O (9 : 1 : 0.1—8 : 2 : 0.2)] and Bondapak ODS (70—85% MeOH) to give **3** (21.3 mg), **6** (23.6 mg) which were identified by comparing their ^{1}H- and ^{13}C-NMR spectral data with those of chilianosides C and F, respectively, along with the starting material **1** (32.0 mg).

Reduction of 3 and 6 Triphenylphosphine (20 mg) was added to a solution of **3** (10 mg) in MeOH (10 ml). After stirring at room temperature for 4 h, the solution was evaporated to dryness under reduced pressure, then subjected to silica gel chromatography [$CHCl_3$–MeOH–H_2O (8 : 2 : 0.2)] to afford **8** (4.0 mg) whose ^{1}H- and ^{13}C-NMR data are completely identical with those of chilianoside H. Reduction of **6** (13 mg) in the manner similar to that described for **4** yielded **11** (5.6 mg) whose ^{1}H- and ^{13}C-NMR data are completely identical with those of chilianoside K.

Acknowledgements This work was supported by a Grant-in-Aid for Scientific Research (No. 07672273) from the Ministry of Education, Science, Sports and Culture of Japan, and by a Yamamura Yuichi Memorial WAKAN-YAKU Research Grant.

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