Five New Diterpenoids from *Pseudolarix kaempferi*

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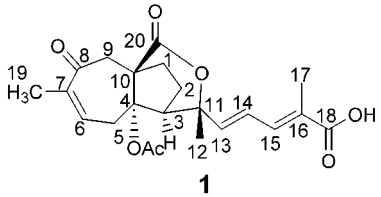
Received January 11, 2002

Five new diterpenoids, pseudolaric acids F (**1**), G (**2**), and H (**3**), 2′,3′-dihydroxy-1′-propoxypseudolarate B (**4**), and 6′-*O*-acetylpseudolaric acid B *O*-*β*-D-glucopyranoside (**5**), along with nine known diterpenoids, pseudolaric acids A, B, and C_1, deacetylpseudolaric acid C_2, deacetylpseudolaric acid A, methyl pseudolarate A, methyl pseudolarate B, pseudolaric acid A-*O*-*β*-D-glucopyranoside, and pseudolaric acid B-*O*-*β*-D-glucopyranoside, were isolated from the root bark of *Pseudolarix kaempferi*. Their structures and stereochemistry were elucidated mainly by spectral data, especially 2D NMR techniques.

A series of novel diterpenoids[1] and triterpenoids[2] have been isolated from the root bark of *Pseudolarix kaempferi* Gordon (Pinaceae), known as "Tu-Jin-Pi" in traditional Chinese medicine and used for the treatment of skin diseases caused by fungal infections.[1a] A number of triterpenoids[3] have been isolated from the fruits of this plant. Some of the compounds obtained from this species, such as pseudolaric acids A and B, pseudolarolide B, and isopseudolarifuroic acids A and B, have shown potent cytotoxic[4] and antimicrobial[1b,2b,5] potencies. In the present investigation, five new diterpenoids, namely, pseudolaric acids F (**1**), G (**2**), and H (**3**), 2′,3′-dihydroxy-1′-propoxypseudolarate B (**4**), and 6′-*O*-acetylpseudolaric acid B-*O*-*β*-D-glucopyranoside (**5**), along with nine known diterpenoids, pseudolaric acids A, B, and C_1, deacetylpseudolaric acid C_2, deacetylpseudolaric acid A, methyl pseudolarate A, methyl pseudolarate B, pseudolaric acid A-*O*-*β*-D-glucopyranoside, and pseudolaric acid B-*O*-*β*-D-glucopyranoside, were isolated from the root bark of *Pseudolarix kaempferi*. The structures and stereochemistry of **1**−**5** were elucidated by spectral data interpretation. Deacetylpseudolaric A, methyl pseudolarate B, and methyl pseudolarate A were isolated from the root bark of *P. kaempferi* for the first time.[1,6]



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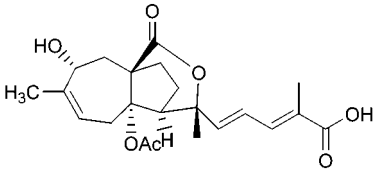

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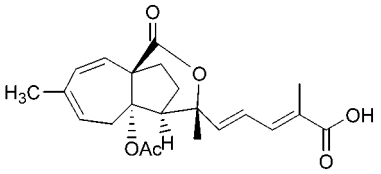

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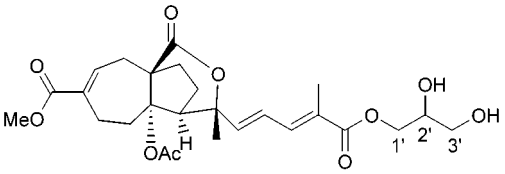

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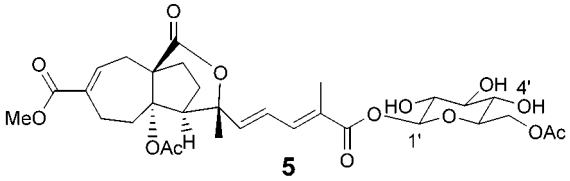

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Pseudolaric acid F (**1**), with the molecular formula $C_{22}H_{26}O_7$ as determined by HREIMS (*m*/*z* 384.1571 [M − H_2O]$^+$, calcd 384.1573), was obtained as a white amorphous powder. The ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2) data showed the presence of four methyls, four methylenes, five methines, and nine quaternary carbons. The ^{1}H NMR, ^{13}C NMR (DEPT), and HMQC spectra permitted the characterization of one disubstituted and two trisubstituted double bonds, one ketone group, three ester carbonyls, and two oxygenated quaternary carbons. Four proton signals (each 3H) at *δ* 1.64 (s), 1.73 (d), 1.89 (d), and 2.02 (s) in the ^{1}H NMR spectrum were assigned to four methyl groups. The singlet methyl group at *δ* 2.02 that correlated with one of the carbonyl groups in the HMBC spectrum showed the occurrence of an acetyl group. These data indicated that compound **1** was most likely an analogue of pseudolaric acid A, which also was obtained in the present investigation. Analysis of the ^{1}H−^{1}H COSY, HMQC, and HMBC confirmed that **1** has the same basic skeleton as pseudolaric acid A. The absence of a molecular ion and the presence of a weak characteristic ion at *m*/*z* 342 [M − AcOH] in the EIMS, a typical observation for the derivatives of pseudolaric acid A,[7] further supported this conclusion. Comparison of the ^{1}H NMR and ^{13}C NMR spectra of compound **1** with those of pseudolaric acid A[1a,b] suggested that the two compounds possess the same side chain.

The oxygenated quaternary carbon signal at *δ* 84.8 was assigned unambiguously to C-11 in **1** from the correlation with the proton signal of H-12 at *δ* 1.64 in the HMBC spectrum. Consequently, the other oxygenated quaternary carbon signal at *δ* 88.2 was assigned to C-4 bearing an

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10.1021/np0200010 CCC: $22.00
Published on Web 06/06/2002

Table 1. ^{1}H NMR Data of Compounds **1**−**5**[a,b]

proton	**1**	**2**	**3**	**4**	**5**
1	1.93 (m) 1.81 (m)	1.81 (2H, m)	1.99 (m) 1.92 (m)	1.80 (2H, m)	1.91 (2H, m)
2	1.88 (2H, m)	1.79 (2H, m)	2.02 (m) 1.92 (m)	1.80 (2H, m)	1.87 (2H, m)
3	3.27 (d, 5.0)	3.14 (br d, 4.4)	3.19 (d, 6.2)	3.31 (m)	3.40 (br d, 3.0)
4					
5	3.45 (ddd, 17.3, 7.0, 1.0) 3.07 (ddd, 17.3, 4.9, 1.6)	3.41 (br d, 14.0) 2.34 (dd, 14.0, 4.8)	3.55 (dd, 16.4, 11.2) 2.56 (dd, 16.4, 2.7)	3.05 (dd, 13.7, 5.8) 1.67 (m)	3.21 (dd, 14.1, 5.6) 1.65 (m)
6	6.09 (m)	5.12 (m)	5.38 (ddd, 11.2, 2.7, 1.1)	2.66 (2H, br d, 6.6)	3.02 (dd, 15.4, 5.6) 2.28 (m)
7					
8		4.46 (br d, 10.9)	5.74 (dd, 12.3, 1.1)	7.09 (m)	7.36 (m)
9	3.04 (d, 16.0) 2.88 (d, 16.0)	2.26 (br d, 13.5) 1.85 (m)	5.70 (d, 12.3)	2.79 (dd, 15.6, 6.3) 2.19 (m)	2.81 (dd, 15.2, 9.5) 2.63 (m)
10					
11					
12	1.64 (s)	1.59 (s)	1.61 (s)	1.57 (s)	1.50 (s)
13	6.22 (d, 15.2)	6.18 (d, 15.1)	6.20 (d, 15.2)	6.22 (d, 15.1)	5.76 (d, 15.0)
14	6.56 (dd, 15.2, 11.4)	6.56 (dd, 15.1, 11.5)	6.57 (dd, 15.2, 11.8)	6.53 (dd, 15.1, 11.5)	6.59 (dd, 15.0, 11.9)
15	7.19 (d, 11.4)	7.18 (d, 11.5)	7.19 (d, 11.8)	7.24 (d, 11.5)	7.41 (d, 11.9)
16					
17	1.89 (d, 1.2)	1.90 (d, 1.1)	1.90 (d, 1.1)	1.91 (d, 1.3)	1.78 (s)
18					
19	1.73 (d, 1.3)	1.76 (d, 0.7)	0.89 (m)		
20					
CH_3CO-4	2.02 (s)	1.95 (s)	1.91 (s)	2.28 (s)	2.14 (s)
CH_3O				3.65 (s)	3.62 (s)
1′				4.20 (m) 4.11 (m)	6.45 (d, 7.3)
2′				3.87 (m)	4.19−4.31 (4H, m)
3′				3.56 (2H, d, 3.2)	
4′					
5′					
6′					4.94 (dd, 16.9, 11.9) 4.78 (dd, 16.9, 12.1)
CH_3CO-6′					1.83 (s)

[a] Data expressed in ppm, with *J* values in Hz. [b] Compounds **1**−**4** were measured in acetone-d_6, and compound **5** was recorded in pyridine-d_5.

acetoxy group. The two proton signals at δ 3.45 and 3.07 were assigned to the H_2-5 by the correlations with the C-4 and the carbon signal at δ 130.3 (C-6) in the HMBC spectrum. The carbon signal at δ 33.4 was then attributable to C-5 by the correlations with the two analogous proton signals of H_2-5 in the HMQC spectrum. The olefinic proton signal at δ 6.09 was assigned to H-6 by the HMBC spectral correlation with C-5 and C-4. In turn, the olefinic carbon signal at δ 130.3 was assigned to C-6 by the correlation with H-6 in the HMQC spectrum, with the H-6 signal also having a correlation with the carbon signal at δ 141.3 assignable to C-7, indicating the presence of a double bond between C-6 and C-7. A quaternary carbon signal at C-10 at δ 55.2 could also be distinguished. The proton signals of H-1, H-2, and H-3 were identified by the correlations in the ^{1}H−^{1}H COSY spectrum and confirmed by correlations between H-1 and C-10 and between H-3 and C-4 in the HMBC spectrum, and in consequence, the assignments for C-1, C-2, and C-3 were made on the basis of HMQC spectral correlations with H-1, H-2, and H-3, respectively. The proton signals at δ 3.04 and 2.88 were assigned to the H_2-9 protons by the correlations with C-10 in the HMBC spectrum. The carbon signal at δ 201.1 for one ketone group was allocated to C-8 from the correlations with the H_2-9 proton signals. The proton signal for a methyl group at 1.73 (3H, d, J = 1.3 Hz) was attributable to the H_3-19 protons from the correlations with C-6, C-7, and C-8 in the HMBC spectrum. The carbonyl signal at δ 173.8 was assigned to C-20 on the basis of the correlations of H_2-1 signals (δ 1.93 and 1.81) and H_2-9 signals (δ 3.04 and 2.88). Therefore, the structure of pseudolaric acid F was elucidated as **1**.

Table 2. ^{13}C NMR Data of Compounds **1**−**5**[a,b]

carbon	**1**	**2**	**3**	**4**	**5**
1	33.6	34.7	33.1	33.8	33.2
2	25.5	24.2	27.0	24.8	24.4
3	49.3	49.1	49.2	50.1	49.3
4	88.2	84.5	87.2	90.3	89.6
5	33.4	31.7	33.6	31.4	30.7
6	130.3	115.1	121.7	28.2	20.2
7	141.3	147.9	135.0	135.2	134.5
8	201.1	68.4	128.3	142.7	141.9
9	44.1	37.7	128.7	20.5	27.8
10	55.2	57.5	60.3	56.0	55.2
11	84.8	84.4	84.6	84.4	83.4
12	28.1	28.0	28.2	28.5	27.9
13	144.5	145.2	144.9	145.5	145.0
14	122.5	122.3	122.3	121.9	120.9
15	137.3	137.5	137.3	137.8	138.2
16	129.3	129.1	129.3	128.6	127.4
17	12.8	12.8	12.8	20.6	12.2
18	169.8	169.8	169.8	168.5	166.7
19	20.5	19.4	25.9	168.4	167.6
20	173.8	174.2	173.2	173.5	172.7
CH_3*CO*-4	170.2	170.2	169.9	170.3	169.3
CH$_3$CO-4	21.4	21.3	21.4	21.6	21.1
CH_3O				52.1	51.5
1′				66.7	95.8
2′				70.6	73.8
3′				63.7	77.8
4′					70.6
5′					75.8
6′					64.1
CH_3*CO*-6′					170.4
CH$_3$CO-6′					20.3

[a] Data expressed in ppm. [b] Compounds **1**−**4** were measured in acetone-d_6, and compound **5** was recorded in pyridine-d_5.

Pseudolaric acid G (**2**) exhibited the molecular formula $C_{22}H_{28}O_7$ as determined by HREIMS (*m/z* 386.1764 [M − H_2O]$^+$, calcd 386.1729) combined with ESIMS (*m/z* 427 [M + Na]$^+$). The molecular composition showed that compound **2** had two more hydrogen atoms than **1**. The ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2) data showed the presence of four methyls, four methylenes, six methines, and eight quaternary carbons. Comparison of the ^{1}H and ^{13}C NMR data of **2** with those of **1** suggested that both compounds have very similar structures. This was supported by the absence of a molecular ion and the presence of a weak characteristic ion at *m/z* 344 [M − AcOH]$^+$ in the EIMS of **2**.[7] Further analysis of the spectral data of these two compounds revealed that the only difference was the presence of an additional hydroxyl group in **2** instead of one of the ketone groups in **1**. The olefinic proton signal at δ 5.12 correlated with the C-5, C-4, and C-7 in the HMBC spectrum was assigned to H-6, indicating the presence of a double bond between C-6 and C-7. The proton signal at δ 4.46 was allocated to the oxygenated tertiary carbon at 68.4 bearing a hydroxyl group from the HMQC spectrum and was then assigned to H-8 on the basis of correlations with C-6 and C-9, suggesting the hydroxyl group was attached to C-8. A NOESY spectrum was performed to determine the stereochemistry of the hydroxyl group. The H-8 proton signal at δ 4.64 (br d, J = 10.9 Hz) correlated with H-5β at δ 2.34 (dd, J = 14.0, 4.8 Hz) and H-9β at δ 1.85 (m) and was assigned a β-configuration, indicating that OH-8 was in the α-orientation. In the NOESY spectrum, H-5β could be differentiated from H-5α by the correlations with H-3α since only H-5α was observed to correlate with the latter proton signal. The H-8β was also correlated with the H-9β resonance at δ 2.26, which could be distinguished from the H-9α signal at δ 1.85, because H-9β was more deshielded by the C-20 lactone carbonyl and shifted downfield. Accordingly, the structure of pseudolaric acid G was determined as **2**.

Pseudolaric acid H (**3**), with a molecular formula $C_{22}H_{26}O_6$ as determined by HREIMS ([M]$^+$ *m/z* 386.1712, calcd 386.1729), was isolated as an amorphous powder. The ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2) data showed the presence of four methyls, three methylenes, seven methines, and eight quaternary carbons. From the ^{1}H NMR, ^{13}C NMR, and HMQC spectra, the occurrence of two disubstituted double bonds and two trisubstituted double bonds, three carbonyls, and two oxygenated quaternary carbons was evident. The absence of a molecular ion and the presence of a characteristic weak ion at *m/z* 326 [M − AcOH]$^+$ in the EIMS suggested that **3** is a pseudolaric acid A analogue.[7] The ^{1}H NMR and ^{13}C NMR spectral data of **3** indicated that this compound possesses the same side chain as **1** and **2**. Analysis of spectral data of compound **3** showed the presence of one more disubstituted double bond and the absence of a hydroxyl group at C-8 on comparison with compound **2**. The presence of a double bond between C-8 and C-9 was then determined on the grounds of HMBC NMR spectral correlations. The olefinic signal at δ 5.70 was assigned to H-9 on the basis of the correlations with the quaternary carbon signal at δ 60.3 (C-10) and the carbonyl signal at δ 173.2 (C-20). The olefinic proton signal at δ 5.74 was consequently assigned to H-8 from the correlations between itself and two olefinic carbon signals at δ 135.0 (C-7) and 128.7 (C-9), as well as the quaternary carbon signal at δ 84.6 (C-10). The assignments for H-8 and H-9 were confirmed by their strong correlations between the analogous two protons in the HMQC spectrum. The occurrence of a double bond between C-6 and C-7 was also revealed by the HMBC spectrum, in which one olefinic signal at δ 5.38 was assigned to H-6 judging from the correlation with the oxygenated quaternary carbon signal of C-4 at δ 87.2 and the carbon signal of C-5 at δ 33.6. The structure of pseudolaric acid H was thus elucidated as **3**.

2′,3′-Dihydroxy-1′-propoxypseudolarate B (**4**) was assigned the molecular formula $C_{26}H_{34}O_{10}$ by HREIMS (*m/z* 488.2051 [M − H_2O]$^+$, calcd 488.2046) and ESIMS (*m/z* 529 [M + Na]$^+$). The ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2) data showed the presence of four methyls, seven methylenes, six methines, and nine quaternary carbons. The ^{1}H NMR, ^{13}C NMR, and MS data were used to infer that **4** is a derivative of pseudolaric acid B.[1a,b,5] Analysis of the ^{1}H NMR, ^{13}C NMR, and EIMS data of **4** indicated the presence of a 2′,3′-dihydroxy-1′-propoxyl group, which was supported by correlations between H_2-1′ (δ 4.20, 4.11), H-2′ (δ 3.87), and H_2-3′ (δ 3.56) in the HMQC spectrum. In the HMBC spectrum, the oxygenated methylene proton signals at δ 4.20 and 4.11 assigned for the two H_2-1′ protons were correlated with the carbonyl signal of C-18 at δ 168.5, indicating that the 2′,3′-dihydroxy-1′-propoxyl group is attached to C-18 in the side chain to form a glyceroyl ester of pseudolaric acid B. A characteristic ion at *m/z* 372 [M − $C_3H_6O_2$ − AcOH]$^+$ in the EIMS supported this conclusion. The structure of compound **4** was therefore elucidated as 2′,3′-dihydroxy-1′-propoxypseudolarate B.

6′-*O*-Acetylpseudolaric acid B-*O*-β-D-glucopyranoside (**5**) was assigned the molecular formula $C_{31}H_{40}O_{14}$ by HREIMS (*m/z* 414.1662 [M − AcOH − 162 (glc)]$^+$ corresponding to $C_{23}H_{26}O_7$, calcd 414.1679) and ESIMS (*m/z* 659 [M + Na]$^+$). The ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2) data showed the presence of five methyls, eight methylenes, 11 methines, and 10 quaternary carbons. Comparison of the spectral data of compound **5** with those of pseudolaric acid B-*O*-β-D-glucoside[5] inferred that the structures of the two compounds were very similar. However, the proton signals at δ 4.94 (dd, J = 16.9, 11.9 Hz) and 4.78 (dd, J = 16.9, 12.1 Hz) for the two protons of H_2-6′ were shifted downfield about 1 ppm by the effect of acylation, clearly indicating that one acetoxyl group was linked to the C-6′ position. The structure of compound **5** was hence assigned as 6′-*O*-acetylpseudolaric acid B-*O*-β-D-glucopyranoside.

Pseudolaric acids A, B, and C_1, deacetylpseudolaric acid C_2, deacetylpseudolaric acid A, methyl pseudolarate A, methyl pseudolarate B, pseudolaric acid A-*O*-β-D-glucopyranoside, and pseudolaric acid B-*O*-β-D-glucopyranoside were identified on the basis of spectral data[1,2b,6] and comparison with authentic samples (co-TLC).

Experimental Section

General Experimental Procedures. Optical rotations were determined on a Perkin-Elmer 341 polarimeter. UV spectra were measured on a Shimadizu UV-210A spectrometer. IR spectra were recorded on a Perkin-Elmer 577 spectrometer with KBr disks. NMR spectra were measured on a Bruker AM-400 spectrometer with TMS as internal standard. EIMS (70 eV) and ESIMS were carried out on a Finnigan MAT 95 mass spectrometer and a Finnigan LCQDECA instrument, respectively. All solvents used were of analytical grade (Shanghai Chemical Plant, Shanghai, People's Republic of China). Silica gel (200−300 mesh) was used for column chromatography, and a precoated silica gel GF254 plate (Qingdao Haiyang Chemical Plant, Qingdao, People's Republic of China) was used for TLC. C_{18} reversed-phase silica gel (150−200 mesh, Merck) and MCI gel (CHP20P, 75−150 μm, Mitsubishi Chemical Industries Ltd.) were also used for column chromatography.

Plant Material. The root bark of *Pseudolarix kaempferi* (Pinaceae) was collected in Jiangxi Province of the People's

Republic of China and identified by Professor Zeng-Tao Wang of Shanghai Chinese Traditional Medical University, where a voucher specimen has been deposited in the Herbarium (accession number TJP-1999-1Y).

Extraction and Isolation. The dried root bark (10 kg) of *P. kaempferi* was ground and percolated with 95% ethanol. After filtration and removal of the solvent, the ethanol extract was dissolved in 2 L of 5% $NaHCO_3$ solution to make a suspension and immediately extracted with ethyl acetate to give a neutral EtOAc-soluble fraction (40 g). The aqueous solution was then treated with 5% HCl solution to about pH 6 and extracted with EtOAc again to afford an acidic EtOAc-soluble fraction (78 g). The acidic EtOAc-soluble fraction was subjected to silica gel column chromatography using a gradient solvent system of petroleum−EtOAc (4:1 to 2:1), and then chloroform−methanol (10:1 to 0:1), and seven major fractions 1−7 were collected. The first of these fractions was then chromatographed sequentially over a MCI gel CHP 20P column (MeOH−water, 6:4 to 10:0), a silica gel column (petroleum−EtOAc, 3:1 to 2:1), and a reversed-phase silica gel column (MeOH−water, 7:3) to afford pseudolaric acid F (**1**) (21.3 mg), pseudolaric acid G (**2**) (3.3 mg), pseudolaric acid H (**3**) (4.6 mg), methyl pseudolarate A (10 mg), and methyl pseudolarate B (690 mg). Fraction 2 was recrystallized from petroleum ether−acetone (4:1) to afford pseudolaric acid A (630 mg). The filtrate was condensed to give a yellow residue, which was then column chromatographed over silica gel eluted with petroleum−EtOAc (2:1) to afford deacetylpseudolaric acid A (3 mg). Fraction 3 was recrystallized from petroleum ether−actone (4:1) to yield pseudolaric acid B (9.6 g), and the filtrate was subjected to reversed-phase silica gel column chromatography eluted with MeOH−water (5:5) to afford pseudolaric acids C_1 (53.8 mg) and deacetylpseudolaric acid C_2 (25 mg). Fraction 4 was chromatographed sequentially over a silica gel column eluted with chloroform−methanol (50:1 to 10:1), a MCI gel CHP 20P column eluted with methanol−water (8:2), and a reversed-phase C_{18} silica gel column eluted with methanol−water (6:4) to provide compounds **4** (4.7 mg) and **5** (67 mg). Fraction 5 was subjected to silica gel column chromatography eluted with a mixture of chloroform−methanol (10:1) to yield a major compound, pseudolaric acid B-*O*-*β*-D-glucopyranoside (9.54 g), and a minor component. The minor compound, which contained a small amount of impurity, was then subjected to passage over a reversed-phase C_{18} silica gel column eluted with methanol−water (5:5) to afford pseudolaric acid A-*O*-*β*-D-glucopyranoside (270 mg).

Pseudolaric acid F (1): white amorphous powder; $[\alpha]^{20}_D$ +25.1° (*c* 0.93, Me_2CO); UV (MeCN) λ_{max} (log ϵ) 258 (4.52) nm; IR (KBr) ν_{max} 3446, 2926, 1741, 1680, 1640, 1613, 1373, 1236, 1171, 1049, 982, 945, 754 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; EIMS *m*/*z* 384 (1), 368 (5), 342 (7), 298 (30), 283 (10), 237 (10), 225 (17), 199 (20), 188 (18), 160 (19), 149 (26), 117 (19), 91 (35), 77 (21), 60 (100), 57 (32); HREIMS *m*/*z* $[M - H_2O]^+$ 384.1571 ($C_{22}H_{24}O_6$, calcd 384.1573).

Pseudolaric acid G (2): white amorphous powder; $[\alpha]^{20}_D$ −17.4° (*c* 0.71, Me_2CO); UV (MeCN) λ_{max} (log ϵ) 259 (4.42) nm; IR (KBr) ν_{max} 3446, 2970, 1739, 1720, 1641, 1610, 1448, 1371, 1244, 1173, 1057, 1026, 982, 955, 754 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; ESIMS *m*/*z* 427 $[M + Na]^+$, 831 $[2M + Na]^+$; EIMS *m*/*z* 386 (1), 368 (4), 344 (19), 326 (58), 298 (18), 281 (60), 265 (30), 245 (37), 211 (25), 199 (70), 161 (71), 147 (82), 133 (60), 105 (70), 91 (100), 77 (55), 55 (50); HREIMS *m*/*z* $[M - H_2O]^+$ 386.1764 ($C_{22}H_{26}O_6$, calcd 386.1729).

Pseudolaric acid H (3): gum; $[\alpha]^{20}_D$ +11.5° (*c* 0.56, Me_2CO); UV (MeCN) λ_{max} (log ϵ) 257 (4.67) nm; IR (KBr) ν_{max} 3446, 2976, 1740, 1641, 1612, 1439, 1369, 1240, 1157, 1043, 981 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; ESIMS *m*/*z* 409 $[M + Na]^+$, 795 $[2M + Na]^+$; EIMS *m*/*z* 386 (1), 327 (3), 326 (18), 309 (4), 308 (20), 298 (4), 290 (3), 283 (5), 282 (24), 281 (21), 267 (25), 265 (5), 221 (4), 195 (8), 183 (47), 172 (16), 168 (11), 145 (11), 144 (45), 143 (19), 129 (13), 128 (12), 105 (11), 91 (16), 68 (100); HREIMS *m*/*z* $[M]^+$ 386.1712 ($C_{22}H_{26}O_6$, calcd 386.1729).

2′,3′-Dihydroxy-1′-propoxypseudolarate B (4): white amorphous powder; $[\alpha]^{20}_D$ −18.3° (*c* 0.46, Me_2CO); UV (MeCN) λ_{max} (log ϵ) 261 (4.45) nm; IR (KBr) ν_{max} 3435, 2953, 1740, 1707, 1632, 1608, 1446, 1383, 1232, 1165, 752 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; ESIMS *m*/*z* 529 $[M + Na]^+$, 1035 $[2M + Na]^+$; EIMS *m*/*z* 488 (2), 447 (2), 414 (10), 372 (5), 355 (10), 354 (33), 342 (4), 334 (11), 328 (16), 316 (19), 310 (14), 296 (12), 295 (10), 284 (15), 274 (14), 260 (16), 257 (13), 242 (38), 224 (36), 191 (45), 137 (37), 128 (30), 131 (100), 117 (32), 115 (31), 109 (36), 105 (44), 91 (83), 61 (79); HREIMS *m*/*z* $[M - H_2O]^+$ 488.2051 ($C_{26}H_{32}O_9$, calcd 488.2046).

6′-*O*-Acetylpseudolaric acid B-*O*-*β*-D-glucopyranoside (5): white amorphous powder; $[\alpha]^{20}_D$ −7.2° (*c* 0.77, Me_2CO); UV (MeCN) λ_{max} (log ϵ) 265 (4.47), 205 (4.59) nm; IR (KBr) ν_{max} 3446, 2953, 1736, 1717, 1716, 1643, 1610, 1444, 1371, 1279, 1232, 1074, 750 cm^{-1}; ^1H NMR, see Table 1; ^{13}C NMR, see Table 2; ESIMS *m*/*z* 659 $[M + Na]^+$; EIMS *m*/*z* 414 (10), 372 (18), 342 (19), 328 (16), 296 (21), 260 (100), 224 (45), 191 (39), 169 (17), 131 (38), 91 (27), 77 (15); HREIMS *m*/*z* $[M - AcOH - 162]^+$ 414.1662 ($C_{23}H_{26}O_7$, calcd 414.1679).

Acknowledgment. Financial support of the National Scientific Foundation (for J.-M.Y., 30025044) and the Shanghai Municipal Scientific Foundation for Fundamental Research (for J.-M.Y., 00JC14053) is gratefully acknowledged. We thank Zeng-Tiao Wang of Shanghai Chinese Traditional Medical University for identification of the plant material.

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NP0200010