March 2006 *Chem. Pharm. Bull.* **54**(3) 297—300 (2006) 297

Three New and Antitumor Anthraquinone Glycosides from *Lasianthus acuminatissimus* MERR

Bin LI*,[a,b] Dong-Ming ZHANG,[c] Yong-Ming LUO,[a] and Xiao-Guang CHEN[c]

[a] *Jiangxi University of Traditional Chinese Medicine; Nanchang 330006, People's Republic of China:* [b] *Beijing University of Traditional Chinese Medicine; Beijing 100029, People's Republic of China: and* [c] *Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College; Beijing 100050, People's Republic of China.*

Received July 5, 2005; accepted October 28, 2005

Three new anthraquinone glycosides, lasianthuoside A (1), B (2), and C (3), were isolated from the root of *Lasianthus acuminatissimus* MERR., The structural elucidation of these anthraquinones was mainly established on the basis of 1D and 2D NMR and HR-MS spectroscopic analysis. Ten known compounds, damnacanthol (4), damnacanthol 11-methyl ether (5), damnacanthol-3-*O*-β-D-primeveroside (6), asperuloside (7), asperulosidic acid (8), deacetyl asperulosidic acid (9), a nonglycosidic iridoid (10), 2,6-dimethoxy-4-hydroxyphenol-1-*O*-β-D-glucopyranoside (11), tachioside (methoxyhydroquinone-4-*O*-β-D-glucopyranoside) (12), and isotachioside (methoxyhydroquinone-1-*O*-β-D-glucopyranoside) (13) were also identified for the first time from this plant in the course of the phytochemical and spectroscopic investigation. In addition to this report, a preliminary evaluation of 13 compounds in treating rheumatoid arthritis and antitumor effects of six anthraquinones are presented.

Key words *Lasianthus acuminatissimus*; lasianthuoside A; lasianthuoside B; lasianthuoside C; iridoid; bioactivity

Lasianthus acuminatissimus MERR. is a plant of the Rubiaceae family, distributed in the southern provinces of China. It is used in traditional Chinese folk medicine for the treatment of rheumatoid arthritis. However, the investigations on the chemical constituents of plant have been few, studies were limited to species taxonomy, and no compound was reported.[1,2] In a search for the active constituents in the treatment of rheumatoid arthritis, the acetone extract of the roots was chromatographed on a silica gel column, and the obtained eluates were subjected to chemical investigation leading to the isolation and the structural elucidation of three new anthraquinone glycosides, lasianthuoside A (**1**), B (**2**), and C (**3**). Ten known compounds, damnacanthol (**4**),[3,4] damnacanthol 11-methyl ether (**5**),[5] damnacanthol-3-*O*-β-D-primeveroside (**6**),[3] asperuloside (**7**),[6] asperulosidic acid (**8**),[6] deacetyl asperulosidic acid (**9**),[6] a nonglycosidic iridoid (**10**),[7] 2,6-dimethoxy-4-hydroxyphenol-1-*O*-β-D-glucopyranoside (**11**),[8] tachioside (**12**),[9] and isotachioside (**13**)[9] are also reported for the first time from this plant. In addition to a preliminary evaluation in treating rheumatoid arthritis, we found that the iridoid glycosides are the bioactive compounds of the plant. The antitumor activity of six anthraquinones against human 2780 cells was also evaluated, and the three new anthraquinone glycosides showed significant bioactivity.

The HR-FAB mass spectrum of compound **1** showed a molecular ion at *m/z* 469.1087 (Calcd 469.1111) which corresponded to $C_{22}H_{22}O_{10}$ Na [M+Na], while the UV maxima at 203.2, 267.0, and 358.0 nm and IR bands at 3510, 1670, and 1577 cm^{-1} suggested the presence of a hydroxyanthraquinone. A singlet signal at δ_H 3.87 (3H, s), an AB spin system at δ_H 4.58 and 4.67 (each H, d, J=11.0 Hz), and the signals at δ_C 161.52 and 161.37 (two oxygenated aromatic carbons) and δ_C 52.66 (one oxygenated secondary aliphatic carbon) indicated an anthraquinone aglycone with three substituents, a methoxy, a phenolic hydroxyl, and a hydroxymethyl in the ^{1}H-NMR and ^{13}C-NMR spectra. Furthermore, the carbon signals of the glycosyl group suggested a glucose residue attached to one of the hydroxyls. Four aromatic protons in a symmetrical AA′BB′-type pattern indicated that one aromatic ring in the anthraquinone was unsubstituted, and one isolated aromatic proton at δ_H 7.74 exhibited cross-peaks with the carbons at 132.31 (C-2), 161.52 (C-3), 121.19 (C-9a), and 182.77 (C-10) in HMBC, indicating that the other ring was unsubstituted at C-4 and substituted at C-1, C-2, and C-3.

Most anthraquinones isolated from the Rubiaceae have no substituent in one aromactic ring and always have a carbon substituent at position 2 in the other ring.[3] Therefore the hydroxymethyl group in **1** was placed at C-2 on comparative and biogenetic grounds, consistent with the HMBC data. The hydroxymethyl proton signals at δ_H 4.58 and 4.67 exhibited cross-peaks with the carbons at 161.37 (C-1), 132.31 (C-2), 161.52 (C-3), and 63.42 (MeO) further comfirming that they are linked to C-2. The signals at ν 1670 and 1631 cm^{-1} and δ_C 181.13 and 182.77 indicated that the quinine carbonyls were not chelated with the phenol group. Thus the OH had to occupy a β-position of the anthraquinone, and thus the phenolid hydroxyl had to be at C-3, and the methoxy group was placed at C-1 because the methoxy proton exhibited a cross-peak with the carbon at 161.37 (C-1) in HMBC. The δ_C of MeO (63.42, *i.e.*, greater than 60) was in agreement with an *ortho*-disubstituted arrangement.

To locate the glucosylated hydroxyl group (OH-3 or OH-11), the ^{13}C-NMR data of **1** were compared with those of the reference compound damnacanthol-11-*O*-β-D-glucoside.[3] Several significant differences involving the δ_C values of **1** were noted: 1) C-11 was shifted to a higher field (δ_C 52.66, cf. δ_C 59.2 for reference) and C-2 to a lower field (δ_C 132.31, cf. δ_C 125.2 for reference). Such changes were in agreement with the α-carbinyl carbon of the aglycone moiety being lower field shifted (*ca.* 7), while the β-carbon is higher field shifted after glycosylation.[10,11] 2) The upfield shift of C-3 and downfield shift of C-9a in **1** relative to the corresponding signals in the reference compound can be attributed to the substituted OH-3 and its shielding effect on the para carbon C-9a. 3) C-1′ was shifted to higher field (δ_C 101.74, cf. δ_C 103.0 in the reference compound), and this change was due to the increased shielding of the anomeric carbon from the

---

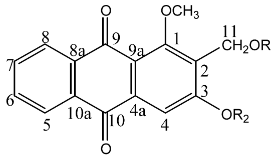
* To whom correspondence should be addressed. e-mail: lily7077@tom.com

secondary pyranoside in C-11 to the tertiary pyranoside in C-3.[10] Comparing **1** with the known compound damnacanthol-3-*O*-*β*-D-primeveroside (compound **6**), their aromatic carbonyl and glucose carbonyl data were rather similar, which strongly suggested glycosylation was located in C-3.

Furthermore, the δ of the anomeric proton of **1** was shifted to δ 5.11 from δ 4.31 in the reference compound, which also strongly suggested that C-1′ was linked to a phenolic oxygen rather than an alcoholic one. The above data confirmed that OH-3 was glucosylated and that OH-11 was free. Based on the *J* value (7.0 Hz) of the doublet of H-1′, the anomeric configuration of **1** was *β*, and the ^{13}C-NMR signals of the sugar portion correspond well to a D-glucose.[9] The proposed structure was further comfirmed by HMBC. The proton at δ 5.11 (H-1′) exhibited cross-peaks with the carbon at δ 161.52 (C-3), indicating the glycosylation was occupied to C-3. Thus **1** was deduced to be 3-hydroxy-1-methoxy-2-hydroxymethyl-9,10-anthraquinone-3-*O*-*β*-D-glucopyranoside, *i.e.*, lasianthuoside A. All the ^{1}H and ^{13}C data of the aglycone were unambiguously assigned by means of HMBC.

The HR-FAB mass spectrum of compound **2** showed a molecular ion at *m*/*z* 461.1427 (Calcd 461.1447) which corresponded to $C_{23}H_{25}O_{10}$ [M+1], while UV maxima absorption at 207.2, 265.8, and 358.0 nm and IR bands at 3435, 1674, and 1599 cm^{-1} suggested the presence of a hydroxyanthraquinone. The ^{1}H- and ^{13}C-NMR and DEPT spectral data of **2** showed that it was similar to compound **1**, except for the additional presence of a MeO (δ_H at 3.29, δ_C at 58.63). HMBC indicated that the protons at δ 4.53 and δ 4.63 (CH_2O) exhibited cross-peaks with the carbons at δ 162.23 (C-3), 128.48 (C-2), and 58.63 (MeO), and the protons at δ 3.29 with the carbon at δ 62.66 (CH_2O), indicated that this MeO is substituted at C-11. The structure of this new anthraquinone glycoside we designated lasianthuoside B was thus 3-hydroxy-1-methoxy-2-methoxymethylanthraquinone 3-*O*-*β*-D-glucopyranoside.

The HR-FAB mass spectrum of compound **3** showed a molecular ion at *m*/*z* 592.1855 (Calcd 592.1870) which corresponded to $C_{28}H_{33}O_{14}$ (M+1), while UV maxima at 202.4, 268.4, and 358.0 nm and IR bands at 3450, 1668, and 1585 cm^{-1} suggested the presence of a hydroxyanthraquinone. Data for compound **3**, when compared with **2**, revealed the presence of additional signals for the sugar D-xylose (the anomeric proton and carbon are at 5.16 and 104.81, respectively).[3,9] Comparison of the sugar carbon res-



	R1	R2
1	H	glc
2	OMe	glc
3	OMe	prim
4	OMe	H
5	H	H
6	H	prim

prim=6-*O*-*β*-D-xylopyranosyl-*β*-D-glucopyranosyl

Fig. 1. The Structures of Compounds **1**—**6**

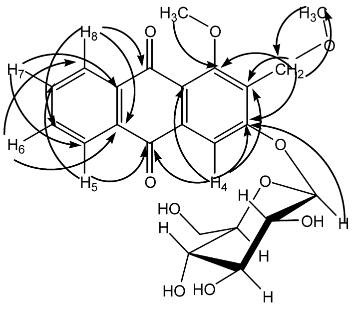
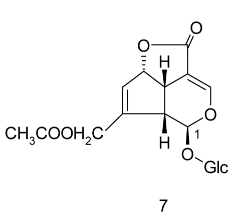


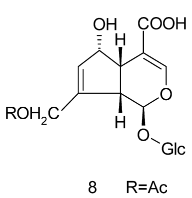
Fig. 2. Main H–C Long-Range Correlations Observed from the HMBC Spectrum of **2**

Table 1. ^{13}C-NMR Spectral Data for Compounds **1**—**6** (DMSO-d_6)

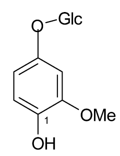
C	**1**	**2**	**3**	**4**	**5**	**6**
1	161.37	161.60	161.54	161.67	159.97	160.65
2	132.31	128.48	128.52	128.82	122.35	131.61
3	161.52	162.23	162.22	162.12	162.59	160.71
4	109.76	109.34	109.49	109.76	112.32	109.16
4a	136.42	136.94	137.00	135.37	136.48	135.73
5	126.93	126.96	127.03	126.11	126.70	126.28
6	134.38	134.41	134.36	133.38	133.20	133.62
7	135.10	135.44	135.42	134.61	134.24	134.67
8	127.44	127.46	127.43	126.68	127.16	126.69
8a	135.39	135.10	135.09	134.56	134.90	134.36
9	181.13	181.05	181.06	179.99	181.09	180.42
9a	121.19	120.35	120.96	117.87	118.51	120.50
10	182.77	182.79	182.88	182.56	182.84	182.15
10a	132.76	132.75	132.81	132.03	132.65	132.07
11	52.66	62.66	63.49	52.08	69.25	51.92
OMe_1	63.42	63.49	62.67	62.41	62.04	62.71
OMe_2		58.63	58.63		59.24	
1′	101.74	101.38	101.38			100.96
2′	74.05	73.96	73.90			73.23
3′	76.73	77.01	76.85			75.85
4′	70.11	70.07	70.19			69.47
5′	78.09	78.08	77.12			76.38
6′	61.17	61.13	68.75			68.02
1″			104.81			104.05
2″			73.98			73.28
3″			76.45			75.69
4″			69.89			69.18
5″			66.34			65.62



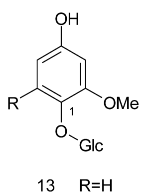
7



8 R=Ac
9 R=H



12



13 R=H
11 R=OMe

Fig. 3. The Structures of Compounds **7**—**13**

Table 2. HMBC Spectral Data for Compounds **1**—**3**

Position	**1** (δ_H)	HMBC data of **1** (δ_C)	**2** (δ_H)	HMBC data of **2** (δ_C)	**3** (δ_H)	HMBC data of **3** (δ_C)
OMe_1	3.87 s	1	3.89 s	1	3.86 s	1
OMe_2			3.29 s	11	3.31 s	11
11α	4.58 (d, 11.0)	1, 2, 3	4.53 (d, 10.0)	1, 2, 3, OMe_2	4.50 (d, 11.0)	1, 2, 3, OMe_2
11β	4.67 (d, 11.0)	1, 2, 3	4.63 (d, 10.0)	1, 2, 3, OMe_2	4.60 (d, 11.0)	1, 2, 3, OMe_2
4	7.74 s	2, 3, 10, 9a	7.75 s	2, 3, 10, 9a	7.74 s	2, 3, 10, 9a
5	8.13 m	7, 10	8.14 m	7, 10	8.14 m	7, 10
6	7.86 m	8, 10a	7.87 m	8, 10a	7.85 m	8, 10a
7	7.94 m	5, 8a	7.94 m	5, 8a	7.93 m	5, 8a
8	8.23 m	6, 9, 10a	8.19 m	6, 9, 10a	8.18 m	6, 9, 10a
1′	5.11 (d, 7.0)	3	5.07 (d, 5.5)	3	5.11 (d, 7.0)	3
1″	—	—	—	—	5.16 (d, 5.0)	6′

Table 3. ^{13}C-NMR Spectral Data for Compounds **7**—**9** (CD_3OD)

C	**7**	**8**	**9**
1	99.08	99.29	101.46
3	149.34	152.53	155.44
4	105.25	107.79	108.41
5	36.37	40.75	42.68
6	84.73	73.32	75.37
7	127.75	131.89	129.87
8	143.29	142.61	151.41
9	44.18	44.65	45.79
10	61.12	62.01	62.77
11	170.18	167.89	170.85
Aco	21.22	20.63	
	170.63	170.00	
1′	99.08	98.89	100.38
2′	73.67	73.07	74.90
3′	77.07	76.47	78.39
4′	70.69	69.86	71.56
5′	77.95	77.06	77.73
6′	61.79	60.98	61.66

onances with DEPT and HMBC data revealed that the signal at 68.75 assigned to C-6′ of glucose was shifted downfield by *ca.* 7.6 from that of compound **2** (δ_C 61.13). Such changes were in agreement with the α-carbinyl carbon of the glycosyl moiety being lower field shifted (*ca.* 7) after glycosylation.[10,11] Thus the terminal xylose moiety is attached to the glucose at C-6 through (1→6)-β-linkage (J=5.0 Hz). HMBC indicated that protons at δ 4.50 and δ 4.60 (CH_2O) exhibited cross-peaks with the carbons at δ 161.54 (C-1), 162.22 (C-3), 128.52 (C-2), and 58.63 (MeO), the protons at δ 3.86 with the carbon at δ 161.54 (C-1) indicated that the MeO was substituted at C-1, the other MeO protons at δ 3.31 with the carbons at δ 63.49 (CH_2O) indicated that it was substituted at C-11. The proton at δ 5.11 (H-1′) exhibited cross-peaks with the carbon at δ 162.22 (C-3), showing that glucosylation was located at C-3. Thus **3** was identified as 3-hydroxy-1-methoxy-2-methoxymethylanthraquinone-3-*O*-β-D-primeveroside, *i.e.*, lasianthuoside C.

Ten known compounds, damnacanthol (**4**), damnacanthol 11-methyl ether (**5**), damnacanthol-3-*O*-β-D-primeveroside (**6**), asperuloside (**7**), asperulosidic acid (**8**), deacetyl asperulosidic acid (**9**), a nonglycosidic iridoid (**10**), 2,6-dimethoxy-4-hydroxyphenol-1-*O*-β-D-glucopyranoside (**11**), tachioside (**12**), and isotachioside (**13**) were also isolated and characterized by comparison of their spectral data (NMR, MS) with the literature values.

Compounds **1**—**6** were evaluated against human 2780 cells, three new anthraquinone glycosides (compounds **1**, **2**, **3**) showed inhibitory effects on human 2780 cells with estimated IC_{50} values of 0.84, 1, and less than 0.1 μg/ml, respectively, while the other two anthraquinone aglycones showed no significant inhibition. This indicates that the glycosyl moiety is a necessary substituent for the antitumor potency. On the other hand, inhibitory values for compound **3** were higher than for compound **2**. The results may suggest that the more glycosyl groups attached, the higher the activity against human ovarian cancer. In this respect, this prelimnary biological evaluation of anthraquinones from *Lasianthus acuminatissimus* MERR. appears promising since some compounds reveal activity against human 2780 cells.

A preliminary evaluation in treating rheumatoid arthritis with the present compounds showed that compounds **7** and **9** exhibit an inhibitory effect on the release of TNF-α from cultured mouse peritoneal macrophages with IC_{50} values of

Table 4. IC_{50} Values (μg/ml) for Inhibitive on Human 2780 Cells of Compounds **1**—**6**

Compound	Inhibitory (%)	IC_{50} (μg/ml)
1	60.2	0.84
2	50.8	1
3	73.5	<0.1
4	2.7	>10
5	35.4	>10
6	43.8	>10

Table 5. Effect on Release of TNF-α from Cultured Mouse Peritoneal Macrophages of Compounds **1**—**13**

	OD	Inhibitory (%)	IC_{50} (μg/ml)
Vacancy	0.632±0.018		
LPS (0.5 mg/ml)	0.447±0.050		
1	0.501±0.017	29.3	>10
2	0.470±0.040	12.6	>10
3	0.505±0.017	32.0	>10
4	0.522±0.007	40.6	>10
5	0.527±0.006	42.9	>10
6	0.534±0.002	46.9	>10
7	0.570±0.014	66.5	0.52
8	0.508±0.036	33.3	>10
9	0.545±0.009	53.1	1
10	0.531±0.040	45.7	>10
11	0.491±0.018	23.7	>10
12	0.451±0.027	2.5	>10
13	0.464±0.039	9.4	>10

0.52 and 1 μg/ml, respectively, while the other compounds did not show any significant inhibition. Because the release of TNF-α is one of the main factors in rheumatoid arthritis, the results may suggest that iridoid glycosides are the bioactive compounds of the plant in the treatment of rheumatoid arthritis. Inhibitory values for compound **7** were higher than those of **9**, yet **8** showed no significant activity. Because the polarity of **8** is between that of **7** and **9**, this may suggest that esterification of all or none of OH is beneficial for the activity and half-esterification is not favorable. The amount iridoid glycosides is sufficient in the plant, and further investigations are underway in our laboratory.

Experimental

Melting points were determined with an XT4-100X micromelting point apparatus and are uncorrected. UV spectra were recorded on a Shimadzu UV-260 spectrophotometer. IR spectra were obtained in KBr on a Perkin Elmer 683 infrared spectrometer. ^{1}H- and ^{13}C-NMR spectra and 2D NMR experiments (HMQC, HMBC) were recorded on a Inova-500 spectrometer at 500 and 125 MHz, respectively, with tetramethylsilane as an internal standard. HR-FAB-MS and EI-MS were determined on an Autospec-Ultima ETOF spectrometer. ESI-MS were obtained on an Agillent 1100 Series LC/MSD Trap mass spectrometer separately. Silica gel (Qing Dao Hai Yang Chemical Group Co., Qing Dao, China) was used for column chromatography, Si gel GF$_{254}$ (Qing Dao Hai Yang Chemical Group Co.) was used for TLC, and compounds were detected by UV at 254 nm. Porous polymer gel was purchased from Shandong Lukang Chemical Factory, and Sephadex LH-20 from Bei Jing Jin Ou Ya Chemical Company, respectively. The optical density was measured with a Model 312 microtiter plate reader purchased from Biotech Research Laboratories, Inc., Rockville, MD, U.S.A.

Plant Material The roots of *L. acuminatissimus* Merr. were collected from Yushan, Jiangxi, China, during December 2003, which were identified by Professor Xue-wen Lai (Jiangxi University of traditional Chinese medicine). A voucher is deposited in the Chinese Pharmacy Department, Jiangxi University of traditional Chinese medicine, Nanchang, China.

Extraction and Isolation Air-dried and powdered roots of the plants (10 kg) were refluxed with 95% EtOH (50 l) three times, and the alcoholic extracts were concentrated and deposited to yield **4** (350 mg) and recrystallizeded with MeOH. The concentration was successively extracted with petroleum ether, ethyl ether, ethyl acetate, acetone, and *n*-butanol, and the ethyl ether extracts yielded **5** (30 mg). The acetone extracts were combined and evaporated to dryness (43 g). All of these extracts were subjected to silica gel column chromatography (1500 g) using mixtures of $CHCl_3$/MeOH/H_2O (8 : 2 : 0.1). Fractions 6 and 7 were combined and recrystallized with methanol to give **6** (130 mg). Other fractions were monitored by TLC and similar fractions combined to afford fractions A (6.1 g), B (2.9 g), C (0.8 g), D (3.3 g), E (2.0 g), F (1.2 g), G (3.1 g), and H (5.6 g). Fraction A was refractioned on a Sephadex LH-20 column using 60% MeOH to give a total of 26 fractions (20 ml each). Fractions 2—4 and 8—15 were combined to yield fractions A_1 (2.6 g) and A_2 (0.65 g), respectively. A_1 was further chromatographed on a 130 g silica gel column eluted with $CHCl_3$/MeOH (100 : 2, 9 : 1) to give 50 fractions. Fractions 34—36 contained **1** (73 mg), and fractions 45—46 contained **3** (25 mg). Fraction A_2 was chromatographed on a 35 g silica gel column [eluted with $CHCl_3$/MeOH (100 : 2, 9 : 1)] to give 30 fractions. Fractions 19—20 contained **2** (55 mg). Fraction B was chromatographed on a reverse-phase silica gel column (eluted with 5% MeOH) to yield 30 fractions. Fractions 8 and 9 gave **10** (25 mg), and, fractions 25—29 gave **11** (10 mg). Fraction C was refractionated on a reverse-phase silica gel column eluted with 15% MeOH, and fractions 8—9 gave **12** (17 mg), and fractions 10 and 11 gave **13** (20 mg). Fraction D contained **7** (750 mg), which was recrystallized with MeOH. Fraction E was refractioned on a reverse-phase silica gel column eluted with 20% MeOH, and fractions 5—8 contained **8** (300 mg). Fraction F was chromatographed on a reverse-phase silica gel column eluted with 5% MeOH to yield 30 fractions. Fractions 8—10 gave **9** (460 mg).

Biological Testing Cell viability was determined using the MTT assay kit using following the manufacturer's protocol. OVCAR-2780 cells were cultured in 96-well plates. Experimental groups were exposed to anthraquinones at final concentrations of 0.1, 1, and 10 μm/ml (diluted with RPMI-1640) for 48 h, and RPMI-1640 of an equal volume was added to the control group. MTT 0.5% was the added to each well, and the plates were incubated for 4 h. After the cells were incubated in 100 μl of dimethylsulfoxide, the absorbance was measured with a microtiter plate reader (Model 312, Biotech Research Laboratories) at a test wavelength of 550 nm and a reference wavelength of 690 nm.The optical density (OD) was calculated as absorbance at the reference wavelength minus that of the test wavelength. Percent viability was calculated as (OD of drug-treated sample/control OD)$\times$100.

L929 cells were cultured in 96-well plates at a concentration of 1×10^5 cells/ml, the plates were incubated at 37 °C for 24 h, the upper solution was discarded, experimental groups were exposed to the samples (diluted with RPMI-1640) for 20 h, and RPMI-1640 of an equal volume was added to the control group. MTT 5 mg/ml was added to each well, and the plates were incubated for 4 h. After the cells were incubated in 100 μl of the dimethylsulfoxide for about 10 min, and the absorbance was measured with a microtiter plate reader (Model 312, Biotech Research Laboratories) at a test wavelength of 570 nm and a reference wavelength of 690 nm.The OD was calculated as absorbance at the reference wavelength minus that of the test wavelength. Percent viability was calculated as (OD of LPS irritant—drug-treated sample/OD of LPS irritant—control)$\times$100.

Lasianthuoside A (**1**): Yellow needles, mp 223—225 °C (MeOH). HR-FAB-MS: m/z=469.1087 {Calcd for [$C_{22}H_{22}O_{10}Na$ (M+Na)], 469.1111}. ESI-MS m/z (%): 469 $[M+Na]^+$ (100), 429 $[M-OH]^+$ (5), 285 $[M-glc+1]^+$ (15). UV λ_{max}^{MeOH} nm (log ε): 203.2 (4.00), 267.0 (4.05), 326.6 (3.00), 358.0 (3.03). IR ν_{max}^{KBr} cm^{-1}: 3510 (OH, free), 3390 (OH, br), 2922 (CH_2), 1670 (C=O), 1631, 1577 (Ar), 1331, 1282, 1109, 1078, 1028 (C–O), 972, 764, 715. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ: 8.13—8.23 (2H, m, H-5, 8), 7.86—7.94 (2H, m, H-6, 7), 7.74 (1H, s, H-4), 5.11 (1H, d, J=7.0 Hz, H-1′), 4.58, 4.67 (each 1H, d, J=11.0 Hz, AB system, H-11), 3.89 (3H, s, MeO), 3.73 (1H, d, J=11.0 Hz, H-6′β), 3.24—3.56 (m, glucose protons).

Lasianthuoside B (**2**): Yellow needles, mp 224—226 °C (MeOH). HR-FAB-MS: m/z=461.1427 {Calcd for [$C_{23}H_{25}O_{10}$ (M+1)], 461.1447}. ESI-MS m/z (%): 483 $[M+Na]^+$ (100), 469 $[M+Na-CH_2]^+$ (4), 455 $[M+Na-2CH_2]^+$ (1), 320 $[M+Na-1-glc]^+$ (8). UV λ_{max}^{MeOH} nm (log ε): 207.2 (3.96), 265.8 (4.06), 331.6 (3.06), 358.0 (2.99). IR ν_{max}^{KBr} cm^{-1}: 3435 (OH, br), 1674 (C=O), 1599, 1539, (Ar), 1385, 1282, 1080, 1043 (C–O), 669. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ: 8.14—8.19 (2H, m, H-5, 8), 7.87—7.94 (2H, m, H-6, 7), 7.75 (1H, s, H-4), 5.07 (1H, d, J=5.5 Hz, H-1′), 4.53, 4.63 (each 1H, d, J=10.0 Hz, AB system, H-11), 3.89 (3H, s, MeO), 3.29 (3H, s, MeO), 3.25—3.70 (m, glucose protons).

Lasianthuoside C (**3**): Yellow needles, mp 238—240 °C (MeOH). HR-FAB-MS: m/z=593.1855 {Calcd for [$C_{28}H_{33}O_{14}$ (M+1)], 593.1870}. ESI-MS m/z (%): 615 $[M+Na]^+$ (100). UV λ_{max}^{MeOH} nm (log ε): 202.4 (3.95), 268.4 (4.12), 358.0 (3.02); IR ν_{max}^{KBr} cm^{-1}: 3450 (OH, br), 1668 (C=O), 1585, 1558 (Ar), 1346, 1286, 1078 (C–O), 789, 758, 669. ^{1}H-NMR (DMSO-d_6, 500 MHz) δ: 8.14—8.18 (2H, m, H-5, 8), 7.85—7.93 (2H, m, H-6, 7), 7.74 (1H, s, H-4), 5.16 (1H, d, J=5.0 Hz, H-1″), 5.11 (1H, d, J=7.0 Hz, H-1′), 4.50, 4.60 (each 1H, d, J=11.0 Hz, AB system, H-11), 3.96 (1H, d, J=10.5 Hz, H-6′β), 3.86 (3H, s, MeO), 3.31 (3H, s, MeO), 2.97—3.96 (m, sugar protons).

Acknowledgements The item is supported by Chinese national natural scientific fund (No. 20262003). The authors would like to thank Professor Jian-bei Li and Wen-yi He for recording the mass and NMR spectra, respectively, and thank Mr. You-shou Yu for collecting the plants.

References

1) Zhu H., *Acta Phytotaxonomica Sinica*, **32**, 49—81 (1994).
2) Zhu H., *Acta Phytotaxonomica Sinica*, **39**, 116—150 (2001).
3) Lu Y., Xu P. J., Chen Z. N., Lui G. M., *Phytochemistry*, **49**, 1135—1137 (1998).
4) Zhao H., Biehl E., *J. Nat. Prod.*, **58**, 1970—1974 (1995).
5) Chiriboga X., Gianluca G., Magnaghi I., Finzi P. V., Zanoni G., Vidari G., *J. Nat. Prod.*, **66**, 905—909 (2003).
6) Peng J. N., Feng Y. Z., Li G. Y., Liang X. T., *Acta Pharm. Sin.*, **32**, 908—913 (1997).
7) Takeda Y., Shimidzu H., Mizuno K., Inouchi S., Masuda T., Hirata E., Shinzato T., Aramoto M., Otsuka H., *Chem. Pharm. Bull.*, **50**, 1395—1397 (2002).
8) Ishimaru K., Supo H., Satake M., Shimomora K., *Phytochemistry*, **29**, 3823—3825 (1990).
9) Inoshiri S., Sasaki M., Kohda H., Otsuka H., Yamasaki K., *Phytochemistry*, **26**, 2811—2814 (1987).
10) Kasai R., Suzuo M., Asakawa J., Tanaka O., *Tetrahedron Lett.*, **18**, 175—178 (1977).
11) Tori K., Seo S., Yoshimura Y., Arita H., Tomita Y., *Tetrahedron Lett.*, **18**, 179—181 (1977).