

## DITERPENOID CONSTITUENTS OF *RABDOSIA LIANGSHANICA*

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**Key Word Index**—*Rabdosia liangshanica*; Labiatae; liangshanin A, B, C, D, E, F, G; inhibitory activities against hepatitis virus.

**Abstract**—The ethereal extract of dried leaves of *Rabdosia liangshanica* were examined. Seven new diterpenoids having an *ent*-kaurane-skeleton, liangshanin A–G were isolated together with sitosterol and stigmasterol, from dried leaves of *Rabdosia liangshanica*. The chemical structures of these new compounds have been elucidated as 7 $\alpha$ ,14 $\beta$ -dihydroxy-*ent*-kaura-1,16-diene-3,15-dione, 7 $\alpha$ -hydroxy-14 $\beta$ -acetoxy-*ent*-kaura-1,16-diene-3,15-dione, 7 $\alpha$ -acetoxy-14 $\beta$ -hydroxy-*ent*-kaura-1,16-diene-3,15-dione, 7 $\alpha$ ,14 $\beta$ ,15 $\alpha$ -trihydroxy-*ent*-kaura-1,16-dien-3-one, 1 $\alpha$ -acetoxy-7 $\alpha$ ,14 $\beta$ -dihydroxy-*ent*-kaur-16-ene-3,15-dione, 7 $\alpha$ ,14 $\beta$ -dihydroxy-12 $\alpha$ -acetoxy-*ent*-kaur-16-ene-3,15-dione and *ent*-11 $\alpha$ ,16 $\alpha$ -epoxykauran-17-ol, respectively, on the basis of detailed spectroscopic analysis, chemical conversions and biogenetic considerations. Some constituents isolated show inhibitory activities against the hepatitis virus.

### INTRODUCTION

*Rabdosia liangshanica* C. Y. Wu et H. W. Li is distributed mainly over southwest Sichuan. Its dried leaves are quite rich in diterpenoids. As a continuation of our phytochemical investigations on *Rabdosia* plants, the structures of seven novel diterpenoids, liangshanin A (1), B (2), C (3), D (4), E (5), F (6) and G (7) were elucidated and two known constituents, sitosterol and stigmasterol were identified. The present communication describes the isolation, structural elucidation and identification of these compounds.

### RESULTS AND DISCUSSION

An ethereal extract of *Rabdosia liangshanica* dried leaves was fractionated by column chromatography on silica gel. Further purification of compounds 1–7 was achieved either by recrystallization, rechromatography on silica gel and silica gel preparative TLC.

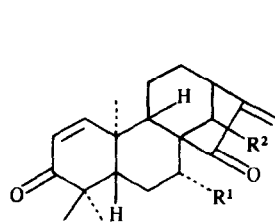
Liangshanin A (1), C<sub>20</sub>H<sub>26</sub>O<sub>4</sub> (M<sup>+</sup> at *m/z* 330), colourless needles, mp 238–240°; [ $\alpha$ ]<sub>D</sub> –192.5° (CH<sub>3</sub>OH; *c* 0.517), showed the presence of three methyl groups, three methylene groups, five methine groups, three quaternary carbons, four olefinic carbons, and two ketonic carbons in the <sup>13</sup>C NMR spectrum. Compound 1 had a five-membered ketone conjugated with an *exo*-methylene group, judging from the following spectral data:  $\lambda_{\max}^{\text{EtOH}}$  230 nm (log  $\epsilon$  4.22);  $\nu_{\max}^{\text{KBr}}$  1725 and 1649 cm<sup>–1</sup>; <sup>1</sup>H NMR  $\delta$  5.47 and 6.19 (each 1H, each *br s*); <sup>13</sup>C NMR  $\delta$  118.0 (*t*) 149.2 (*s*, *exo*-methylene) and 207.0 (ketone). The following spectral data suggest that this compound has an  $\alpha,\beta$ -unsaturated six-membered ketone:  $\nu_{\max}^{\text{KBr}}$  1668 and 1612 cm<sup>–1</sup>; <sup>1</sup>H NMR  $\delta$  5.88 and 7.01 (each 1H, *d*, *J* = 10 Hz); <sup>13</sup>C NMR  $\delta$  159.6 (*d*), 126.7 (*d*) (double bond) and 204.5 (*s*, ketone). The <sup>1</sup>H NMR spectrum showed,

besides the signals of three tertiary methyl groups ( $\delta$  1.17, 1.17 and 1.28), signals due to two methine protons attached to carbons having an oxygen functional group (2 OH): 4.40 (*dd*, 9 and 5 Hz) and 4.83 (*br s*). These data suggest that this compound had the 15-*oxo-ent*-kaurane nucleus as a basic skeleton [1]. In fact, the tetra hydro-compound (10) showed a negative Cotton effect in the ORD.

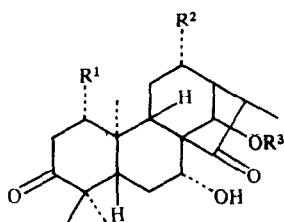
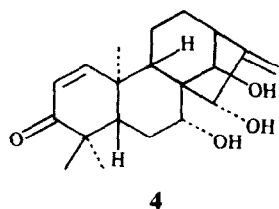
The locations of two oxygen functional groups were deduced as follows. Acetylation of 1 gave the diacetate (9) and the <sup>1</sup>H NMR spectrum showed a signal at  $\delta$  5.98 which suffered abnormal downfield shift compared with the signals due to a proton attached an acetoxy group bearing carbon, indicating that the signal was assigned to 14 $\alpha$ -H. Treatment of 1 with anhydrous acetone in the presence of dry cupric sulphate gave an acetonide (8). Thus, another hydroxy group should be located at the C-7 $\alpha$  position. On the other hand, the carbonyl group of an  $\alpha,\beta$ -unsaturated six-membered ketone was concluded to be located at C-3 by comparison with <sup>13</sup>C NMR data of ericalyxin A and B [2] and glaucocalyxin A and B [3]. Accordingly, the structure of liangshanin A can be represented as 7 $\alpha$ ,14 $\beta$ -dihydroxy-*ent*-kaura-1,16-diene-3,15-dione (1).

Liangshanin B (2) and C (3) showed the following physical data: (2), C<sub>22</sub>H<sub>28</sub>O<sub>5</sub> (M<sup>+</sup> at *m/z* 372), mp 204–210°;  $\lambda_{\max}^{\text{EtOH}}$  230.5 nm (log  $\epsilon$  4.27);  $\nu_{\max}^{\text{KBr}}$  3475, 3170, 1741, 1728, 1660, 1615, 1242, 1087 cm<sup>–1</sup>; (3), C<sub>22</sub>H<sub>28</sub>O<sub>5</sub> (M<sup>+</sup> at *m/z* 372), mp 204–210°;  $\lambda_{\max}^{\text{EtOH}}$  230.5 nm (log  $\epsilon$  4.27);  $\nu_{\max}^{\text{KBr}}$  3480, 1739, 1720, 1655, 1615, 1242, 1085, 940 cm<sup>–1</sup>. Liangshanin B (2) and C (3) have the same oxidation pattern as that of liangshanin A (1) based on the fact that respective acetylation of 2 and 3 afforded the same acetate (9). In the <sup>1</sup>H NMR spectrum, compound 2 showed a signal at  $\delta$  2.01 due to an acetyl group and a signal at  $\delta$  5.93 (1H, *br s*) due to 14 $\alpha$ -H. Consequently, the structure of liangshanin B (2) can be elucidated as 7 $\alpha$ -hydroxy-14 $\beta$ -acetoxy-*ent*-kaura-1,16-diene-3,15-dione. Compound 3 showed a signal at  $\delta$  2.05 due to an acetyl group and a

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	R <sup>1</sup>	R <sup>2</sup>
<b>1</b>	OH	OH
<b>2</b>	OH	OAc
<b>3</b>	OAc	OH
<b>8</b>		
<b>9</b>	OAc	OAc

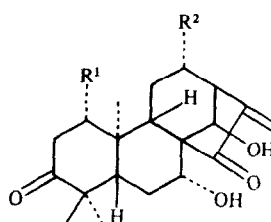


	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
<b>10</b>	H	H	H
<b>13</b>	H	OAc	H
<b>14</b>	H	H	OAc
<b>15</b>	OAc	H	H

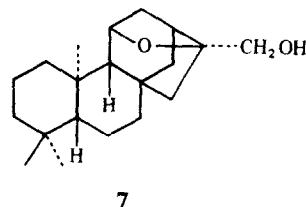
signal at  $\delta$ 5.42 (1H, *dd*,  $J = 9$  and 5 Hz) due to 7 $\beta$ -H. Accordingly, the structure of liangshanin C (3) can be suggested as 7 $\alpha$ -acetoxy-14 $\beta$ -hydroxy-*ent*-kaura-1,16-diene-3,15-dione.

Liangshanin D (4), C<sub>20</sub>H<sub>28</sub>O<sub>4</sub> ( $M^+$  at  $m/z$  332), mp 302–305°, differed from 1 by an additional proton signal at  $\delta$ 4.86 (1H, *br s*) due to 15 $\beta$ -H. Other signal differences noted between 4 and 1 were that exo-methylene signals were shifted upfield from  $\delta$ 5.47 and 6.19 (each 1H, each *br s*) in 1 to  $\delta$ 5.34 (1H, *t*, 1.2 Hz) and 5.71 (1H, *br s*) in 4. Oxidation of 4 with potassium dichromate-sulphuric acid in acetone at room temperature gave 1. Acetylation of 4 gave the triacetate (11). The proposed structure of 4 was supported by the <sup>13</sup>C NMR and <sup>1</sup>H NMR data of 11 [4]. Thus, 4 was determined as 7 $\alpha$ ,14 $\beta$ ,15 $\alpha$ -trihydroxy-*ent*-kaura-1,16-dien-3-one.

Liangshanin E (5), C<sub>22</sub>H<sub>30</sub>O<sub>6</sub> ( $M^+$  at  $m/z$  390), mp 138–140°, gave very similar <sup>1</sup>H and <sup>13</sup>C NMR spectra



	R <sup>1</sup>	R <sup>2</sup>
<b>5</b>	OAc	H
<b>6</b>	H	OAc



(Tables 1 and 2) to those of liangshanin A (1) except that there was no conjugated double bond on ring A and there was an extra acetoxy group: <sup>1</sup>H NMR [ $\delta$ 2.04 (3H, *s*, OAc), 4.91 (1H, *dd*, 8.8 and 2.9 Hz, 1 $\beta$ -H), 3.18 (1H, *dd*, 16 and 8.8 Hz, 2 $\alpha$ -H), 2.14 (1H, *dd*, 16 and 2.9 Hz, 2 $\beta$ -H)] [5]; <sup>13</sup>C NMR [169.8 (*s*) and 21.3 (*q*) (OAc), 79.5 (*d*, 1-C), 42.2 (*t*, 2-C), 214.1 (*s*, 3-C), 14.5 (*q*, 20-C)]. These data suggest that liangshanin E (5) has the structure 1 $\alpha$ -acetoxy-7 $\alpha$ ,14 $\beta$ -dihydroxy-*ent*-kaur-16-ene-3,15-dione.

Liangshanin F (6), C<sub>22</sub>H<sub>30</sub>O<sub>6</sub>, mp 220–222°, had the same  $M_r$  and very similar structure to compound 5. The significant variations between 6 and 5 in the <sup>1</sup>H and <sup>13</sup>C NMR were: <sup>1</sup>H NMR [2.16 (3H, *s*, OAc), 5.20 (1H, *m*,  $W_{1/2} = 10$  Hz, 12 $\beta$ -H), 3.58 (1H, *m*, 13 $\alpha$ -H)]; <sup>13</sup>C NMR [170.0 (*s*) and 21.3 (*q*) (OAc), 23.8 (*t*, 11-C), 74.1 (*d*, 12-C), 53.6 (*d*, 13-C)]. The above mentioned data suggest that liangshanin F had a structure corresponding to 7 $\alpha$ ,14 $\beta$ -dihydroxy-12 $\alpha$ -acetoxy-*ent*-kaur-16-ene-3,15-dione. This presumption was confirmed by the following reaction. Liangshanin F (6) gave the diacetate (12) and dihydro-compound (13).

Liangshanin G (7), C<sub>20</sub>H<sub>32</sub>O<sub>2</sub> ( $M^+$  at  $m/z$  304), mp 146–151° had an IR spectrum which only showed the characteristic absorptions of a hydroxy group at 3260–3140 cm<sup>-1</sup> and ether bond at 1050 cm<sup>-1</sup>. The <sup>13</sup>C NMR data of liangshanin G (7) are summarized in Table 2 and showed the presence of three CH<sub>3</sub>, nine CH<sub>2</sub>, four CH and four tetrasubstituted carbons. Three downfield signals due to carbons connecting with oxygen;  $\delta$ 89.6 (*s*), 76.7 (*d*) and 65.6 (*t*), and two oxygen suggest that this compound has an ether ring. The structure of 7 and a reasonable assignment of <sup>13</sup>C NMR data can be achieved by comparison with similar constituents *ent*-kaurane-16 $\alpha$ ,17-diol [6] and *ent*-11 $\alpha$ ,16 $R$ -epoxy-19-kauranoic acid [7]. Liangshanin G is the first example isolated from the *Rabdosia* genus having an 11 $\alpha$ ,16 $\alpha$ -ether ring. We

Table 1.  $^1\text{H}$  NMR chemical shifts of liangshanin A(1)–G(7)

H	1	2	3	4	5	6	7
1-H	7.01 (d, 10)	7.03 (d, 10)	7.03 (d, 10)	7.12 (d, 10)	4.91 (dd, 8.8, 2.9)		
	5.88	5.90	5.91	5.98	1 $\beta$ -H 2d, 3.18 (dd, 16, 8.8)		
2-H	(d, 10)	(d, 10)	(d, 10)	(d, 10)	2 $\beta$ , 2.14 (dd, 16, 2.9)		
7 $\beta$ -H	4.40 (dd, 9, 5)	4.24 (dd, 9, 5)	5.42 (dd, 9, 5)	4.35 (dd, 10, 5)	4.32 (dd, 9, 5)	4.85 (dd, 10, 6)	
11 $\alpha$ -H							4.43 (t, 5)
						5.20 (m, $W_{1/2} = 10$ )	
12 $\beta$ -H							
13 $\alpha$ -H	3.12 m	3.15 m	3.15 m	3.06 m	3.12 m	3.58 m	2.49 t, 7
14 $\alpha$ -H	4.83 brs	5.93 br s	4.81 br s	4.86 br s	4.79 br s	5.44 br s	2.05 d, 12
17-H <sub>a</sub>	6.19 br s	6.22 br s	6.22 br s	5.71 br s	6.14 br s	6.36 br s	3.77, 3.60,
17-H <sub>b</sub>	5.47 br s,	5.48 br s	5.48 br s	5.34 br s	5.42 br s	5.52 br s	(ABd, 12)
18-Me	1.17 s	1.17 s	1.17 s	1.19 s	1.14 s	1.12 s	0.87 s
19-Me	1.17 s	1.17 s	1.17 s	1.13 s	1.14 s	1.12 s	0.85 s
20-Me	1.28 s	1.40 s	1.29 s	1.22 s	1.14 s	1.21 s	1.09 s
OAc		2.01 s	2.05 s		2.04 s	2.16 s	

Table 2.  $^{13}\text{C}$  NMR chemical shifts of liangshanin A(1)–G(7)

C	1	2	3	5	6	7
1	159.6	158.0	158.0	79.5	38.0	40.8
2	126.7	127.8	127.8	42.2	34.0	18.6
3	204.5	205.4	205.4	214.1	215.6	42.0
4	44.9	45.5	45.5	46.4	47.0	33.1
5	50.7	52.0	52.0	52.6	51.5	56.5
6	30.2	28.8	28.8	28.6	30.8	20.2
7	73.9	73.6	76.6	73.1	73.6	38.2
8	61.2	62.6	62.6	61.2	60.7	44.7
9	48.9	50.4	50.4	48.1	51.2	60.2
10	42.0	42.6	42.6	42.6	38.0	41.1
11	18.6	18.7	18.7	18.9	23.8	76.7
12	31.2	32.8	32.8	30.8	74.1	43.6
13	46.6	45.0	45.0	45.9	53.6	42.4
14	75.7	76.6	73.6	75.2	70.9	37.0
15	207.0	206.4	206.4	207.1	207.3	53.2
16	149.2	146.7	146.7	147.6	145.9	89.6
17	118.0	119.2	119.2	117.9	119.2	65.6
18	29.0	29.4	29.4	28.6	27.3	34.1
19	22.6	23.2	23.2	20.2	21.3	22.2
20	22.3	22.4	22.4	14.5	16.5	18.5
		171.7	171.7	169.8	170.0	
OAc		22.4	22.4	21.3	21.3	

suggest the structure of liangshanin G as *ent*-11 $\alpha$ ,16 $\alpha$ -epoxykauran-17-ol (7).

#### EXPERIMENTAL

Mps: uncorr UV were determined in EtOH. IR were measured in KBr discs. MS were obtained by direct inlet 70 eV.  $^1\text{H}$  and  $^{13}\text{C}$  NMR were recorded at 400.90 and 100.6, 22.63 MHz using TMS as int. standard; chemical shift values were reported in  $\delta$  (ppm) units.

**Plant material.** *Rabdosia liangshanica* leaves were collected in Mianning, Sichuan, China, in September 1986 and identified by Prof. H. W. Li, of our institute where a voucher specimen has been deposited.

**Extraction and isolation of constituents.** Dried and powdered leaves (12 kg) were extracted with Et<sub>2</sub>O and the solvent evapd. The residue (270 g) was dissolved in MeOH and decoloured by activated charcoal when the soln was warm. The transparent light yellow filtrate was concd to ca 1 l and the ppt. which appeared was removed. The MeOH soln was evapd and the residue (153 g) submitted to CC (silica gel) eluting with CHCl<sub>3</sub> and increasing proportions of Me<sub>2</sub>CO–CHCl<sub>3</sub>. Fractions were monitored by TLC. All components were further purified by recrystallization and prep. TLC (silica gel) yielding in order of increasing polarities: 7 (250 mg), 2 and 3 (both together 6 g), 5 (2 g), 6 (100 mg), 1 (9 g), and 4 (150 mg). All data of 1–7 are shown in Tables 1–3. The derivatives were obtained in the usual way.

**Acetonide of liangshanin A (8)** Colourless needles, C<sub>23</sub>H<sub>30</sub>O<sub>4</sub>,  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 1728, 1675, 1646, 1197, 1160, 1115, 935; MS  $m/z$ : 371 [M+1]<sup>+</sup>, 355, 342, 330, 312, 297, 242, 215, 149, 136, 43 (base peak)  $^1\text{H}$  NMR (90 MHz, CDCl<sub>3</sub>):  $\delta$  6.93 (d,  $J = 10$  Hz, 1-H), 5.89 (d,  $J = 10$  Hz, 2-H), 6.20 and 5.44 (each 1H, br s, 17-H<sub>2</sub>), 4.56 (d,  $J = 18$  Hz, 14 $\alpha$ -H), 4.34 (dd,  $J = 10$ , 8 Hz, 7 $\beta$ -H), 3.10 (m, 13 $\alpha$ -H), 1.60 and 1.26 (each 3H, s, 2  $\times$  Me), 1.26 (3H, s, 20-Me), 1.17 (3H, s, 18-Me), 1.13 (3H, s, 19-Me).

**Diacetate of liangshanin A (9).** Colourless needles, C<sub>24</sub>H<sub>30</sub>O<sub>6</sub>,  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 1732, 1670, 1645, 1250; MS  $m/z$ : 415 [M+1]<sup>+</sup>, 387, 372, 354, 330, 312, 294, 266, 136, 83 (base peak)  $^1\text{H}$  NMR (90 MHz, CDCl<sub>3</sub>):  $\delta$  7.03 (d,  $J = 10$  Hz, 1-H), 5.90 (d,  $J = 10$  Hz, 2-H), 6.20 and 5.48 (each 1H, br s, 17-H<sub>2</sub>), 5.98 (br s, 14 $\alpha$ -H), 5.30 (dd,  $J = 8$ , 6 Hz, 7 $\beta$ -H), 3.13 (m, 13 $\alpha$ -H), 1.42 (3H, s, 20-Me), 1.15 (6H, s, 18-, 19-Me).

**Tetrahydroliangshanin A (10).** C<sub>20</sub>H<sub>30</sub>O<sub>4</sub>,  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>: 3240, 1726, 1705, 1113, 1076, 1058, MS  $m/z$ : 334 [M]<sup>+</sup>, 316, 301, 260, 243, 196, 178, 135, 105, 55, 43 (base peak)  $^1\text{H}$  NMR (400 MHz, C<sub>2</sub>D<sub>5</sub>N):  $\delta$  3.18 (q,  $J = 7.0$  Hz, 16-H), 2.58 (m, 13 $\alpha$ -H), 7.81 (br s, OH), 7.12 (br s, OH), 5.13 (br s, 14 $\alpha$ -H), 4.55 (dd,  $J = 9.6$ , 6.0 Hz, 7 $\beta$ -H), 1.18 (3H, d,  $J = 7.2$  Hz, 17-Me), 1.07 (3H, s, 20-Me), 1.06 (3H, s, 18-Me), 1.00 (3H, s, 19-Me).

Table 3. Spectral data of liangshanin A(1)–G(7)

	UV $\lambda_{\text{max}}^{\text{EtOH}}$ (log $\epsilon$ ) nm	IR $\nu_{\text{max}}^{\text{KBr}}$ $\text{cm}^{-1}$	MS $m/z$ (70 eV)
1	230 (4 22)	3250, 1725, 1668, 1649, 1612	330 $[\text{M}]^+$ , 312, 297, 242, 194, 150, 137
2	230.5 (4 27)	3475, 3170, 1741, 1728, 1660, 1615, 1242, 1087	372 $[\text{M}]^+$ , 354, 330, 312, 242, 197, 150, 137
3	230 5 (4 27)	3480, 1739, 1720, 1655, 1615, 1242, 1085, 940	372 $[\text{M}]^+$ , 354, 330, 312, 242, 197, 150, 137
4	207 5 (3.83) 227.5 (3 86)	3300–3220, 1695, 1665, 1650, 1615, 1100, 1055, 900	314 $[\text{M} - \text{H}_2\text{O}]^+$ , 296, 285, 242, 150, 137
5	230 5 (4 02)	3620, 3480, 3410, 3375, 1725, 1700, 1635, 1260	390 $[\text{M}]^+$ , 372, 330, 312, 297, 227, 137
6	229.5 (3 88)	3400, 3350, 1727, 1709, 1690, 1641, 1255, 1221	372 $[\text{M} - \text{H}_2\text{O}]^+$ , 330, 312, 297, 174, 132
7		3260–3140, 2995–2840, 1050	304 $[\text{M}]^+$ , 289, 286, 273, 261, 230, 137

Triacetate of liangshanin D (11).  $\text{C}_{26}\text{H}_{34}\text{O}_7$ ,  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$  1740, 1730, 1670, 1250, 1235, 1225, 1050,  $^1\text{H}$  NMR (400 MHz,  $\text{C}_5\text{D}_5\text{N}$ )  $\delta$  7.11 (*d*,  $J = 10$  Hz, 1-H), 6.38 (*br s*, 14 $\alpha$ -H), 5.99 (*d*,  $J = 10$  Hz, 2-H), 5.87 and 5.33 (each 1H, *br s*, 17-H<sub>2</sub>), 5.23 (*br s*, 15 $\beta$ -H), 5.03 (*dd*,  $J = 11$  2, 3.0 Hz, 7 $\beta$ -H), 2.16, 2.14 and 2.12 (each 3H, *s*, 3  $\times$  OAc), 1.37 (3H, *s*, 20-Me), 1.15 (3H, *s*, 18-Me), 1.07 (3H, *s*, 19-Me), 2.79 (*m*, 13 $\alpha$ -H).

Diacetate of liangshanin F (12).  $\text{C}_{26}\text{H}_{34}\text{O}_8$ ,  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$  1740, 1703, 1650, 1240, 1062, MS  $m/z$ : 372  $[\text{M} - \text{HOAc} - \text{ketene}]^+$ , 354, 330, 312, 297, 174, 161, 43 (base peak)  $^1\text{H}$  NMR (90 MHz,  $\text{C}_5\text{D}_5\text{N}$ )  $\delta$  6.53 (*br s*, 14 $\alpha$ -H), 6.33 and 5.60 (each 1H, *br s*, 17-H<sub>2</sub>), 5.76 (*dd*,  $J = 10$ , 6 Hz, 7 $\beta$ -H), 5.24 (*m*,  $W_{1/2} = 10$ , 12 $\beta$ -H), 3.55 (*m*, 13 $\alpha$ -H), 2.16, 2.13 and 1.93 (each 3H, *s*, 3  $\times$  OAc), 1.49 (3H, *s*, 20-Me), 1.12 (3H, *s*, 18-Me), 1.10 (3H, *s*, 19-Me)

Dihydroliangshanin F (13).  $\text{C}_{22}\text{H}_{32}\text{O}_6$ ,  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$  3400, 1733, 1725, 1685, 1640, 1255, 1220, 1096, 1015,  $^1\text{H}$  NMR (400 MHz,  $\text{C}_5\text{D}_5\text{N}$ )  $\delta$  5.46 (*br s*, 14 $\alpha$ -H), 5.26 (*t*,  $J = 4.2$  Hz, 12 $\beta$ -H), 4.63 (*dd*,  $J = 11$  6, 4.0 Hz, 7 $\beta$ -H), 3.30 (*q*,  $J = 7.0$  Hz, 16-H), 2.84 (*m*, 13 $\alpha$ -H), 2.12 (3H, *s*, OAc), 1.19 (3H, *s*, 20-Me), 1.18 (3H, *d*,  $J = 7.0$  Hz, 17-Me), 1.09 (6H, *s*, 18-, 19-Me).

Tetrahydroliangshanin B (14).  $\text{C}_{22}\text{H}_{32}\text{O}_5$ ,  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$  3505, 1730, 1700, 1303, 1245, 1195, 1100, MS  $m/z$ : 376  $[\text{M}]^+$ , 358, 334, 316, 288, 260, 178, 150, 137, 43 (base peak).  $^1\text{H}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  6.02 (*br s*, 14 $\alpha$ -H), 4.06 (*dd*,  $J = 9$ , 5 Hz, 7 $\beta$ -H), 2.78 (*q*, 7.0, 16-H), 2.58 (*m*, 13 $\alpha$ -H), 2.05 (3H, *s*, OAc), 1.19 (3H, *s*, 20-Me), 1.15 (3H, *d*,  $J = 7.0$  Hz, 17-Me), 1.11 (3H, *s*, 18-Me), 1.08 (3H, *s*, 19-Me).

Dihydroliangshanin E (15)  $\text{C}_{22}\text{H}_{32}\text{O}_6$ ,  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$  3400–3280, 1735, 1710, 1670 1265, 1236, 1115, 970, MS  $m/z$  332  $[\text{M} - \text{HOAc}]^+$ , 314, 299, 196, 178, 150, 137 (base peak)  $^1\text{H}$  NMR (90 MHz,  $\text{C}_5\text{D}_5\text{N}$ )  $\delta$  5.14 (*dd*,  $J = 8.8$ , 2.9 Hz, 1 $\beta$ -H), 5.11 (*br s*, 14 $\alpha$ -H), 4.55 (*dd*,  $J = 10$ , 6 Hz, 7 $\beta$ -H), 3.38 (*dd*,  $J = 16$ , 8.8 Hz, 2 $\alpha$ -

H), 2.37 (*dd*,  $J = 8.8$ , 2.9 Hz, 2 $\beta$ -H), 3.17 (*q*,  $J = 7.0$  Hz, 16-H), 2.59 (*m*, 13 $\alpha$ -H), 2.02 (3H, *s*, OAc), 1.21 (3H, *s*, 20-Me), 1.15 (3H, *d*,  $J = 7.0$  Hz, 17-Me), 1.15 (3H, *s*, 18-Me), 1.04 (3H, *s*, 19-Me)

Acetate of liangshanin G (16).  $\text{C}_{22}\text{H}_{34}\text{O}_3$ ,  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$  1738, 1278, 1240, 1232, 1040, 970, MS  $m/z$  346  $[\text{M}]^+$ , 327, 315, 287, 273, 248 (base peak), 203, 190, 175  $^1\text{H}$  NMR (90 MHz,  $\text{CDCl}_3$ )  $\delta$  4.43 (*t*,  $J = 4$  Hz, 11 $\alpha$ -H), 4.29 and 4.12 (each 1H, *d*,  $J = 11.5$  Hz, 17-H<sub>2</sub>), 2.42 (*t*,  $J = 7.0$  Hz, 13 $\alpha$ -H), 2.09 (3H, *s*, OAc), 1.09 (3H, *s*, 20-Me), 0.87 (3H, *s*, 18-Me), 0.85 (3H, *s*, 19-Me)  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{C}_5\text{D}_5\text{N}$ ) of 11  $\delta$  158.6 (*d*, C-1), 126.4 (*d*, C-2), 203.6 (*s*, C-3), 44.6 (*s*, C-4), 51.0 (*d*, C-5), 26.0 (*t*, C-6), 73.4 (*d*, C-7), 54.9 (*s*, C-8), 47.0 (*d*, C-9), 41.6 (*s*, C-10), 17.7 (*t*, C-11), 33.2 (*t*, C-12), 45.2 (*d*, C-13), 74.5 (*d*, C-14), 76.2 (*d*, C-15), 150.8 (*s*, C-16), 109.4 (*t*, C-17), 28.3 (*q*, C-18), 22.7 (*q*, C-19) 21.6 (*q*, C-20), 3  $\times$  OAc 170.9, 170.5, 170.2, 21.4, 21.2, 20.7

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