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巨花雪胆中的两个新化合物*

陈 亚[1]，邱明华[1**]，古 昆[2]，陈剑超[1]
（1 中国科学院昆明植物研究所植物化学与西部植物资源国家重点实验室，云南 昆明 650204）
2 云南大学化学系，云南 昆明 650091）

摘要：从四川石棉县采集的巨花雪胆（*Hemsleya gigantha*）的根茎中分到2个新化合物，命名为雪胆素G和巨花雪胆皂苷B，通过化学方法和波谱方法鉴定了它们的结构。另外13个已知化合物分别为葫芦素类和雪胆皂苷类化合物，其中β-香树脂醇（**3**）为首次从该属植物中得到。

关键词：巨花雪胆；葫芦科；雪胆素G；巨花雪胆皂苷B；齐墩果酸苷
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A New Cucurbitacin and A New Oleanolic Acid Glycosides from *Hemsleya gigantha* *

CHEN Ya[1], QIU Ming-Hua[1**], GU Kun[2], CHEN Jian-Chao[1]
(1 *State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences*, Kunming 650204, China;
2 *Chemical Department, Yunnan University*, Kunming 650091, China)

Abstract: Two new compounds together with thirteen known compounds were isolated from the roots of *Hemsleya gigantha*. They were named Hemslecins G and Hemsgiganosides B, and their structures were determined on the basis of the spectral and chemical evidences. Compound **3** was first time isolated from the genus.

Key words: *Hemsleya gigantha*; Cucurbitaceae; Hemslecins G; Hemsgiganosides B.

Hemsleya gigantha is mainly distributed in southwestern part of China, especially abundant in Yunnan and Sichuan provinces. The genus plants have been used as herbal medicines in China for treatment of bronchitis, bacillary dysentery, tuberculosis, diabetes, whooping cough and bile duct infection. *Hemsleya gigantha* is a new species that comes from Sichuan province of China. Investigation on this plant led to the isolation of two new compounds, Hemslecins G (**1**), Hemsgiganoside B (**2**) and thirteen known compounds, β-amyrin (**3**) (Cong *et al*, 2000), spinasterol (**4a**), 22, 23-di-

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** Author for correspondence E－mail: mhchiu@public.km.yn.cn
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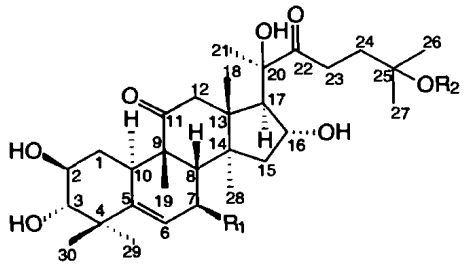
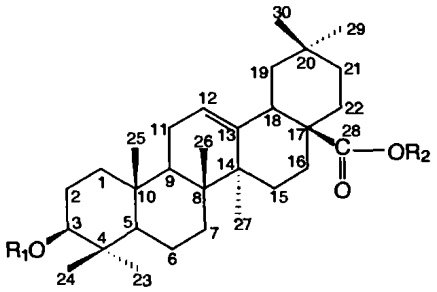
作者简介：陈亚（1964－）女，现为云南农业大学基础与信息工程学院副教授，主要从事有机化学的研究。

hydro-spinasterol (**4b**)(Ding *et al*, 1991; Fan *et al*, 1988), spinasterol-3-O-β-D-glucoside (**5a**), 22, 23-dihydro-spinasterol-3-O-β-D-glucoside (**5b**)(Ding *et al*, 1991; Fan *et al*, 1988), cucurbitacin F (**6**)(Yang *et al*, 1988), 23, 24-dihydro-cucurbitacin F-25-O-acetate (**7**)(Yang *et al*, 2000; Morita *et al*, 1986), cucurbitacin F-25-O-acetate (**8**), 23, 24-dihydro-cucurbitacin F (**9**)(Yang *et al*, 2000), 3-O-(6′-butyl ester)-β-D-glucuropyranosyl-oleanolic acid-28-O-α-L-arabinopyranoside (**10**)(Nie *et al*, 1984; Lin *et al*, 2003), 3-O-(6′-butyl ester)-β-D-glucuropyranosyl-oleanolic acid-28-O-β-D-glucopyranoside (**11**)(Nie *et al*, 1984; Lin *et al*, 2003), oleanolic acid 3-O-β-D-glucuropyranoside (**12**)(Nie *et al*, 1984), 3-O-β-D-glucuropyranosyl-oleanolic acid-28-O-α-L-arabinopyranoside (**13**), 3-O-β-D-glucuropyranosyl-oleanolicacid-28-O-β-D-gluc-uropyranoside (**14**)(Nie *et al*, 1984; Shi *et al*, 1995), 3-O-β-D-glucopyranosyl-(1→2)-β-D-glucuropyranosyl-oleanolicacid-28-O-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside (**15**)(Shi *et al*, 1995).



	R_1	R_2
1	OH	Ac
7	H	Ac

ara: α-L-arabinopyranosyl
glc: β-D-glucopyranosyl
glcUA: β-D-glucuronic acid



	R_1	R_2
2	glcUA	glc$\overset{1-6}{—}$glc
10	$COOCH_2CH_2CH_2CH_3$ | glcUA	ara
11	$COOCH_2CH_2CH_2CH_3$ | glcUA	glc
12	glcUA	H
13	glcUA	ara
14	glcUA	glc
15	glcUA$\overset{1-2}{—}$glc	glc$\overset{1-6}{—}$glc

Fig. 1 Structure of compounds **1**, **2**, **7**, **10**–**15**

Hemslecins G (1) is white powder. Its molecular ion peak in negative HRFAB-MS spectrum at *m/z* 577.3356 ($[M-H]^-$, calcd. 577.3376) suggested the molecular formula of **1** was $C_{32}H_{50}O_9$, which was deduced by the ^{13}C NMR and DEPT. The IR spectrum showed the presence of hydroxy (3525 cm^{-1}) and acetoxy groups (1705, 1251 cm^{-1}). The ^{13}C NMR and DEPT of **1** exhibited 8 methine, 5 methylene and 9 methyl and 10 quaternary carbons, its ^1H NMR displayed 9 methyl signals

at δ_H 1.28, 1.33, 1.47, 1.49, 1.50, 1.58, 1.62, 1.76, 1.87 (s, 9 × CH_3) and olefinic proton signal at δ_H 6.22 (d, 1H, J = 4.8 Hz), these data suggested that compound **1** had the skeleton of cucurbitacin F. The ^{13}C NMR signals of **1** at δ_c 122.5 (CH), 1454 (C) and 215.3 (C), 217.1 (C) indicated the presence of a double oleafinic carbon and two ketone group. Comparison of the ^{13}C NMR spectrum of **1** with **7**, revealed **1** had one more group. The proton of the oxymethine correlating with H－6 in ^{1}H－^{1}H COSY indicated that the hydoxyl group located at C－7. The fact that the signal of C－7 in **1** was upfield shifted from δ_C 86.3 to δ_C 66.3 due to the stronger space-gauche shielding effect of the methane (C－19) with 7β－OH, suggested that 7－OH was at β-orientation. Therefore, the chemical structure of compound **1** was deduced as 7β-hydroxy-23, 24-dihydrocucurbitacin F-25-O-acetate.

Hemsgiganosides B (2), white powder. On acid hydrolysis, **2** gave oleanolic acid which were identified by TLC comparison with the authentic sample. Its molecular formula of $C_{48}H_{76}O_{19}$ was determined by negative HRFAB-MS at *m/z* 955.4870 (calcd. 955.4902). The negative FAB-MS also displayed the peak at $[M-1-162]^-$, $[M-1-162-162]^-$ and $[M-1-162-162-176]^-$, indicating that **2** contains three glucosyl units and a glucuronic acid. Comparison of the ^{13}C NMR spectrum of **2** with that of oleanolic acid, revealed that **2** had the same basic skeleton as oleanolic acid. Two carbon signals at δ_c 88.2, 106.0 indicated 3-linked glucuronide of oleanolic acid (Nie *et al*, 1984). By comparison of ^{13}C NMR data of **2** with that of compound **15** (Nie *et al*, 1984; Shi *et al*, 1995), it was revealed that β-D-glucopyranosyl-(6→1)-β-D-glucopyranoside located at C－28 of oleanolic acid. Based on these results, the of structure of **2** was determined as 3-O-β-D-glucuropyranosyl oleanolic acid 28-O-β-D-gluco-pyranosyl-(1→6)-β-D-glucopyranoside.

The structures of compounds **3－15** were identified by comparing their physical and spectral data with those reported that in literatures.

Experimetal

General All melting points were measured on an XRC-1 micro melting point apparatus and uncorrected. Optical rotation was taken on a SEPA-300 polarimeter. IR spectral data were measured on a Bio-Rad FTS-135 spectrometer with KBr pellets. MS spectra were recorded on a VG Auto Spec-3000 spectrometer. NMR spectra were run on a Bruker AM-400 and a DXB-500 instrument with TMS as internal standard. CC were carried out with silica gel, D101 and TLC silica gel G and silica gel GF254 (Marine Chemical Industry Factory, Qingdao). The spots were visualized by spraying with 20% H_2SO_4 followed by heating.

Plant material The sample of *Hemsleya gigantha* was collected from Shimian county of Sichuan province, China. Specimen was taxonomically identified by Wen-Jin Zhang, Pengxian County Institute for Pharmaceutical Control, Sichuan, China.

Extraction and separation The dried and powdered rhizomes of *Hemsleya gigantha* (1.9 kg) were extracted with hot methnol (65℃) for four times. The extract was evaporated to dryness *in vacuo*. This extract (653 g) was dissolved in H_2O and successively partitioned with petroleum-ester, EtOAc and *n*-BuOH to afford petroleum-ester, EtOAc and *n*-BuOH residues 13, 72, and 301 g respectively, after the solvent was evaporated *in vacuo*, The petroleum ester fraction

was repeatedly chromatographed on silica gel to give **3** (47 mg), **4a** and **4b** (75 mg), **5a** and **5b** (57 mg). The EtOAc fraction was repeatedly chromatographed on silica gel to give **1** (66 mg), **6** (715 mg), **7** (1.472 g), **8** (756 mg), **9** (3.872 g). The *n*-BuOH extract was subjected to macroporous absorption resin D-101, eluting with aq. EtOH, to give three fragments. Fractions 2 – 3 were further purified by repeated column chromatography on silica gel to yield **2** (0.26 mg), **10** (536 mg), **11** (589 mg), **12** (8 mg), **13** (373 mg), **14** (134 mg), **15** (1.262 g).

Compound **1**, white powder, $C_{32}H_{50}O_9$; mp 132 – 138℃; IR ν_{max}^{KBr} cm^{-1}: 3525, 2872, 2890, 1705, 1426, 1369, 1269, 1176, 1119, 1059, 1014, 951, 870, 680; negative FAB-MS *m/z* (%): 577 $[M-1]^-$, 560 $[M-18]^-$; ^1H NMR (C_5D_5N, 500 MHz) δ: 6.01 (1H, s, H – 6), 4.51 (1H, m, H – 7), 1.87, 1.76, 1.62, 1.58, 1.50, 1.49, 1.47, 1.33, 1.28 (27H, s, 9 × CH_3); ^{13}C NMR (C_5D_5N, 125.8 MHz) see Table 1.

Table 1 ^{13}C NMR data for the compounds **1** and **7**

Position	1	7	Position	1	7
1	34.7 (t)	32.9 (t)	17	59.1 (d)	57.6 (d)
2	70.5 (d)	70.1 (d)	18	22.9 (q)	21.4 (q)
3	81.3 (d)	80.4 (d)	19	15.6 (q)	18.7 (q)
4	43.0 (s)	42.0 (s)	20	80.2 (s)	79.0 (s)
5	145.3 (s)	140.7 (s)	21	25.4 (q)	24.3 (q)
6	122.5 (d)	118.8 (d)	22	217.1 (s)	214.2 (s)
7	66.3 (d)	23.5 (t)	23	32.3 (t)	30.7 (t)
8	35.5 (d)	33.6 (d)	24	35.5 (t)	34.5 (t)
9	50.4 (s)	48.3 (s)	25	81.8 (s)	81.6 (s)
10	53.2 (d)	42.5 (d)	26	26.0 (q)	25.5 (q)
11	215.2 (s)	214.0 (s)	27	26.1 (q)	25.8 (q)
12	49.5 (t)	48.6 (t)	28	19.7 (q)	19.6 (q)
13	47.9 (s)	48.1 (s)	29	20.4 (q)	19.8 (q)
14	50.4 (s)	51.0 (s)	30	25.6 (q)	24.4 (q)
15	46.6 (t)	45.2 (t)	31	170.3 (s)	170.9 (s)
16	71.0 (d)	70.4 (d)	32	22.3 (q)	22.0 (q)

(**7** in $CDCl_3$, **1** in C_5D_5N)

Compound **2**, white powder, $C_{48}H_{76}O_{19}$; IR ν_{max}^{KBr} cm^{-1}: 3415, 2938, 2848, 1699, 1606, 1429, 1386, 1160, 1024, 947; negative FAB-MS *m/z* (%): 955 $[M-1]^-$, 793 $[M-1-162]^-$, 631 $[M-1-162-162]^-$, 455 $[M-1-162-162-176]^-$; ^1H NMR (C_5D_5N, 400 MHz) δ: 6.15 (1H, d, J = 8.3 Hz), 5.35 (1H, s), 4.93 (1H, t, J = 5.1 Hz); ^{13}C NMR (C_5D_5N, 100.6 MHz) see Tables 2 and 3.

Compound **3**, white powder, $C_{30}H_{50}O$; mp 155 – 157℃; IR ν_{max}^{KBr} cm^{-1}: 3450, 2938, 1460, 1382, 1035, 995, 659; EI-MS *m/z* (%): 426 $[M]^+$, 411 $[M-CH_3]^+$, 218 (100), 203, 189; ^1H NMR ($CDCl_3$, 500 MHz) δ: 5.16 (1H, m, H – 12), 3.18 (1H, dd, J = 4.5 Hz, H – 3α), 1.11, 0.97, 0.95, 0.91, 0.85, 0.83, 0.80, 0.77 (24H, s, 8 × CH_3) (Cong *et al*, 2000).

Compound **4**, white needle crystals, $C_{29}H_{48}O$ (4a), $C_{29}H_{50}O$ (4b); mp 133 – 136℃; IR ν_{max}^{KBr} cm^{-1}: 3382, 2948, 1465, 1377, 1098, 971, 938, 845, 796, 628; EI-MS *m/z* (%): 414 (100), 412 (100), 399, 397, 369, 300, 273, 271, 255, 246, 231, 147, 119, 107, (Ding *et al*, 1991; Fan *et al*, 1988).

Compound **5**, white needle crystals, 5a ($C_{35}H_{58}O_6$), 5b ($C_{35}H_{60}O_6$); mp 268 – 271℃; EI-MS *m/z* (%): 576 $[Ma]^+$, 574 $[Mb]^+$, 414, 412, 397 (100), 271, 255, 83, 81; IR ν_{max}^{KBr} cm^{-1}: 3450, 2948, 1464, 1376, 1160, 1075, 1028, 971, 892, 845. (Ding *et al*, 1991; Fan *et al*, 1988).

Compound **6**, white gel, $C_{32}H_{48}O_8$; mp 98 – 100℃; IR ν_{max}^{KBr} cm^{-1}: 3444, 2961, 2935, 1692, 1456, 1374, 1286, 1209, 1133, 1053, 1029, 982, 669, 612, 466; ^1H NMR ($CDCl_3$, 400 MHz) δ: 5.59 (1H, d, J = 8.4 Hz), 5.60 (1H, d, J = 4.3 Hz), 1.73, 1.53, 1.14, 1.08, 1.07, 0.95, 0.82, 0.79 (24H, s, 8 × CH_3).

(Yang *et al*, 1988).

Table 2 ^{13}C NMR data for the aglycone moieties of compounds **2** and **10 – 15**

Position	2	10	11	12	13	14	15
1 (t)	37.8	38.9	37.8	38.8	38.5	38.6	38.4
2 (t)	25.6	26.7	27.2	28.4	27.7	26.2	26.5
3 (d)	88.2	89.3	88.2	89.1	90.6	88.9	89.9
4 (s)	38.5	39.6	38.5	39.5	40.2	39.3	39.2
5 (d)	54.9	55.9	54.9	55.9	57.4	55.7	56.1
6 (t)	17.5	19.3	18.3	18.6	20.1	18.4	18.2
7 (t)	32.1	33.3	33.1	33.4	34.3	33.0	33.6
8 (s)	38.9	40.0	39.0	39.8	41.0	39.8	39.3
9 (d)	47.0	48.2	47.1	48.1	48.7	47.9	47.6
10 (s)	35.9	37.1	36.0	37.1	35.7	36.8	36.2
11 (t)	22.7	23.8	22.8	23.9	24.8	23.6	23.2
12 (d)	121.8	123.0	121.9	122.6	124.6	123.0	124.0
13 (s)	143.2	144.3	143.2	144.9	145.7	144.0	144.4
14 (s)	40.7	42.2	40.8	42.1	42.2	41.6	41.3
15 (t)	25.6	28.3	29.9	28.4	27.7	26.2	26.4
16 (t)	22.4	23.9	22.5	23.9	24.8	23.3	23.5
17 (s)	45.3	47.3	46.1	46.8	49.5	46.2	46.3
18 (d)	41.2	41.8	41.2	42.3	43.7	42.0	41.7
19 (t)	46.1	46.4	45.3	46.8	47.8	46.9	46.5
20 (s)	29.7	30.9	31.6	31.1	32.4	30.7	30.2
21 (t)	33.0	34.2	32.2	34.4	34.7	33.9	33.4
22 (t)	32.1	32.8	33.1	32.2	34.3	33.0	33.4
23 (q)	27.2	28.3	27.2	29.6	29.6	28.2	28.3
24 (q)	16.0	17.0	15.9	16.7	18.6	16.9	16.6
25 (q)	14.6	15.6	14.6	15.5	17.1	15.4	15.0
26 (q)	16.5	17.6	16.5	17.5	18.9	17.4	16.2
27 (q)	25.1	26.2	25.1	26.3	25.2	26.0	25.3
28 (q, s)	175.6	176.6	175.4	181.0	178.9	177.5	176.7
29 (q)	31.5	33.3	33.1	33.4	34.3	32.4	31.8
30 (q)	22.7	23.4	22.7	23.0	25.2	23.6	22.2

(**2**, **10 – 15** in C_5D_5N)

Compound **7**, white needle crystals, $C_{32}H_{50}O_8$; mp 338 – 340℃; IR ν_{max}^{KBr} cm^{-1}: 3562, 3413, 2974, 1629, 1465, 1371, 1280, 1182, 988, 968, 809, 857; negative FAB-MS *m/z* (%): 561 $[M-1]^-$, 544 $[M-18]^-$; EI-MS *m/z* (%): 502, 484, 446, 405, 387, 369, 219, 171, 135, 113, 87; ^1H NMR ($CDCl_3$, 500 MHz) δ: 5.56 (1H, d, J = 5.6 Hz), 3.07 (1H, d, J = 14.4 Hz), 1.80, 1.29, 1.28, 1.23, 1.11, 1.02, 0.92, 0.77, 0.76 (27H, s, 9 × CH_3); ^{13}C NMR ($CDCl_3$, 125.8 MHz) see Table 1 (Yang *et al*, 2000; Morita *et al*, 1986).

Compound **8**, white powders, $C_{32}H_{48}O_8$; mp 218 – 220℃; IR ν_{max}^{KBr} cm^{-1}: 3516, 2972, 1707, 1691, 1461, 1372, 1264, 1126, 990, 971, 932, 845, 622; EI-MS *m/z* (%): 500, 482, 457, 405, 387, 369, 351, 327, 219, 171, 135, 119, 96 (100), 69; ^1H NMR (C_5D_5N, 400 MHz) δ: 6.33 (1H, s), 5.71 (1H, d, J = 6.1 Hz), 5.09 (1H, t, J = 7.4 Hz), 3.43 (1H, d, J = 14.4 Hz), 1.87, 1.68, 1.60, 1.55, 1.53, 1.46, 1.31, 1.22, 1.19 (27H, s, 9 × CH_3) (Yang *et al*, 2000).

Compound **9**, white powder, $C_{30}H_{48}O_7$; mp 150 – 155℃; IR ν_{max}^{KBr} cm^{-1}: 3490, 2969, 2886, 1685, 1627, 1461, 1373, 1283, 1212, 1166, 1056, 1028, 987, 855, 758, 672, 631; negative FAB-MS *m/z* (%): 519 $[M-1]^-$, 502 $[M-18]^-$; EI-MS *m/z* (%): 502, 484, 405, 387, 369, 237, 219, 171, 142, 113, 96, 69; ^1H NMR (C_5D_5N, 500 MHz) δ: 5.76 (1H, d, J = 5.6 Hz), 4.39 (1H, d, J = 4.4 Hz), 3.93 (1H, d, J = 4.4 Hz), 1.42, 1.39, 1.34, 1.21, 1.19, 1.08, 1.02, 0.95 (24H, s, 8 × CH_3) (Yang *et al*, 2000).

Compound **10**, white powder, $C_{45}H_{72}O_{13}$; IR ν_{max}^{KBr} cm^{-1}: 3490, 2940, 1730, 1388, 1364, 1259, 1163, 1027, 950, 826, 776, 749, 631, 599; negative FAB-MS *m/z* (%): 819 $[M-1]^-$, 763 $[M-1-56]^-$, 687 $[M-1-132]^-$ (100), 455 $[M-1-132-176-56]^-$; ^1H NMR (C_5D_5N, 400 MHz) δ: 6.26 (1H, d, J = 5.8 Hz, ara H − 1), 4.97 (1H, d, J = 7.7 Hz, glcUA H − 1), 1.31, 1.29, 1.14, 1.12, 0.99, 0.94, 0.88 (21H, s, 7 × CH_3), 0.74 (3H, t, J = 7.4 Hz); ^{13}C NMR (C_5D_5N, 100.6 MHz) see Tables 2 and 3 (Nie *et al*, 1984; Lin *et al*, 2003).

Table 3 ^{13}C NMR data for the sugar moieties of **2** and **10 − 15**

Position		2	10	11	12	13	14	15
3-O-glcUA	1	106.0	107.3	106.3	106.7	107.9	107.0	105.6
	2	77.2	75.5	76.3	75.3	76.7	76.6	78.7
	3	76.6	78.1	77.9	78.1	77.7	75.1	78.0
	4	72.8	73.1	73.2	73.8	72.8	73.9	71.7
	5	77.6	77.4	77.0	77.0	79.5	78.1	76.7
	6	171.6	170.34	169.3	176.9	178.0	176.3	176.3
$COOCH_2CH_2CH_2CH_3$	α		65.0	61.3				
	β		30.0	29.8				
	γ		18.6	17.5				
	δ		13.8	12.7				
glc′ (1→2)	1							105.2
	2							78.0
	3							78.7
	4							71.7
	5							78.0
	6							63.0
ara (1→3)	1							
	2							
	3							
	4							
	5							
28-O-ara	1		95.7			97.3		
	2		71.4			69.5		
	3		73.9			75.4		
	4		66.0			75.0		
	5		66.1			67.6		
28-O-glc	1	94.6		94.8			95.6	95.8
	2	74.4		74.4			74.0	74.0
	3	76.6		72.0			78.8	75.2
	4	70.9		70.3			71.1	71.0
	5	77.2		78.2			79.1	78.4
	6	68.4		63.9			62.2	69.6
glc′ (1→6)	1	104.0						105.2
	2	77.0						73.6
	3	76.2						78.4
	4	70.5						71.1
	5	77.1						78.7
	6	61.1						62.8

Compound **11**, white powder, $C_{46}H_{74}O_{14}$; IR ν_{max}^{KBr} cm^{-1}: 3401, 2925, 2859, 1737, 1461, 1372, 1162, 1070, 627; negative FAB-MS *m/z* (%): 849 $[M-1]^-$, 793 $[M-1-56]^-$ (7), 687 $[M-1-162]^-$ (100), 455 $[M-1-162-176-56]^-$ (21); ^1H NMR (C_5D_5N, 400 MHz) δ: 6.31 (1H, d, J = 8.0 Hz, glc H − 1), 4.99 (1H, d, J = 7.7 Hz, glcUA H − 1), 1.27, 1.25, 1.07, 0.95, 0.90, 0.87, 0.82 (21H, s, 7 × CH_3), 0.75 (3H, t, J = 7.3 Hz); ^{13}C NMR (C_5D_5N, 100.6 MHz) see Tables 2 and 3 (Nie *et al*, 1984; Lin *et al*, 2003).

Compound **12**, white powder, $C_{36}H_{56}O_9$; $[\alpha]_D^{25.3}$ + 8.35℃ (c 0.479, C_5D_5N); IR ν_{max}^{KBr} cm^{-1}: 3950, 2934,

2863, 1692, 1610, 1458, 1436, 1386, 1274, 1208, 1161, 1078, 1029, 982, 948, 635; negative FAB-MS *m/z* (%): 631 (100) $[M-1]^-$, 455 $[M-1-176]^-$; EI-MS *m/z* (%): 456, 412, 248 (100), 203, 163; ^{1}H NMR (C_5D_5N, 400 MHz) δ: 5.68 (1H, m, H-12), 5.60 (1H, m, glcUA H-1); ^{13}C NMR (C_5D_5N, 100.6 MHz) see Tables 2 and 3 (Nie *et al*, 1984).

Compound **13**, white needle crystals, $C_{41}H_{64}O_{13}$; IR ν_{max}^{KBr} cm^{-1}: 3434, 2940, 2836, 1741, 1595, 1463, 1388, 1160, 1075, 776; negative FAB-MS *m/z* (%): 763 $[M-1]^-$, 631 $[M-1-132]^-$, 455 $[M-1-132-176]^-$; ^{1}H NMR (C_5D_5N, 400 MHz) δ: 6.24 (1H, d, J=5.2 Hz), 5.41 (1H, m, H-12); ^{13}C NMR (C_5D_5N, 100.6 MHz) see Tables 2 and 3 (Nie *et al*, 1984; Shi *et al*, 1995).

Compound **14**, white needle crystals, $C_{42}H_{66}O_{14}$; IR ν_{max}^{KBr} cm^{-1}: 3415, 2938, 2848, 1699, 1606, 1429, 1386, 1160, 1024, 947; negative FAB-MS *m/z* (%): 794 $[M-H]^-$, 631 $[M-1-162]^-$, 455 $[M-1-162-176]^-$; EI-MS *m/z* (%): 456, 410, 392, 248, 203, 163; ^{1}H NMR (C_5D_5N, 400 MHz) δ: 6.32 (1H, d, J=7.7 Hz, glc H-1), 5.41 (1H, s, H-12), 5.17 (1H, m, glcUA H-1); ^{13}C NMR (C_5D_5N, 100.6 MHz) see Tables 2 and 3 (Nie *et al*, 1984; Shi *et al*, 1995).

Compound **15**, white powder, $C_{54}H_{86}O_{24}$; negative FAB-MS *m/z* (%): 1117 $[M-1]^-$, 955 $[M-1-162]^-$, 793 $[M-1-162-162]^-$, 631 $[M-1-162-162-162]^-$, 455 $[M-1-162-162-162-176]^-$; ^{1}H NMR (C_5D_5N, 400 MHz) δ: 6.44 (1H, d, J=8.8 Hz), 6.2 (1H, m), 5.91 (1H, m); ^{13}C NMR (C_5D_5N, 100.6 MHz) see Tables 2 and 3 (Shi *et al*, 1995).

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