Chinese Chemical Letters Vol. 12, No. 1, pp. 51–54, 2001

New diterpenoid glucosides from *Siegesbeckia pubescens*

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Abstract: Five new diterpenoids isolated from *Siegesbeckia pubescens*, pubesides A~E, were established as *ent*-2α,15,16-trihydroxypimar-8(14)-en-2-O-β-D-glucopyranoside (1), *ent*-15,16,19-trihydroxypimar-8(14)-en-19-O-β-D-glucopyranoside (2), β-D-glucopyranosyl-*ent*-15,16-dihydroxypimar-8(14)-en-19-oiclate (3), *ent*-2-oxo-15,16,19-trihydroxypimar-8(14)-en-19-O-β-D-gluco-pyranoside (4), *ent*-2-oxo-15,16,19-trihydroxypimar-8(14)-en-19-O-β-D-glucopyranoside-15,16-acetonide (5) by 1D and 2D NMR techniques.

Keywords: *Siegesbeckia pubescens*, new diterpenoid glucosides, pubesides A~E

Plants of the genus *Siegesbeckia* are annual herbs widely distributed in tropical and temperate zones and they are used as a traditional medicine to treat rheumatic arthritis, hypertension, malaria, neurasthenia and snake-bite in China. In previous papers, we reported on five new *ent*-kaurane and *ent*-pimarane diterpenoids, siegesbeckioside, siegesbeckiol and siegesbeckic acid[1], orientalin A and B, and eight know compounds[2,3]. The present paper describes the isolation and structural elucidation of five other new diterpenoid glucosides. n-Butanol extract was fractionated by column chromatography on silica gel and reverse phase silica gel RP-8 successively. Further purification of compounds **1**~**5** was achieved by recrystallization and rechromatography on RP-8.

Pubeside A (**1**), $C_{26}H_{44}O_8$ M 484, was obtained as colorless needles, mp. 265~267°C, $[\alpha]_D^{26}$-36.78 (MeOH, c 0.2477). Its IR spectrum (3400, 1703, 1650, 1075, 1035, 1015 cm^{-1}) revealed the presence of hydroxyl groups and double bond. The comparison of ^1H and ^{13}C NMR spectra of **1** with those of kirenol (**6**) showed the presence of an extra β-D-glucose unit [δ 5.06 (1H, d, 7.8Hz), 102.97 (d), 75.44 (d), 78.42 (d), 71.88 (d), 78.76 (d) and 62.97 (t)] in **1**, the downfield shift of C-2 signal from δ 64.05 ppm in **6** to δ 72.87 in **1,** and the absence of 19-CH_2OH signals in **1**. These facts suggest that **1** is 19-dehydroxy-2-β-D-glucosylkirenol, namely *ent*-2α,15,16-trihy-droxypimar-8(14)-en-2-O-β-D-gluco-pyranoside.

Pubeside B (**2**), $C_{26}H_{44}O_8$ M 484, mp. 257~260°C. The differences of the ^1H and ^{13}C NMR spectra between **1** and **2** are that those of **2** lack 2-CHOH signals, the downfield shift of C-19 and C-4 signals from δ 23.06 and 34.78 ppm in **1** to δ 72.59 and 38.38 in **2**, and the upfield shift of C-18 signal from δ 33.96 ppm in **1** to δ 28.13 in **2**. These facts suggest that **2** is 2-dehydroxy-19-β-D-glucosylkirenol, namely *ent*-15, 16,

19-trihydroxy-pimar-8 (14)-en-19-O-β-D-glucopyranoside.

Pubeside C (**3**), $C_{26}H_{42}O_9$ M 498, mp. 261~263°C. The differences of the ^1H and ^{13}C NMR spectra between **2** and **3** are that those of **3** lack a 19-CH_2OH signals and the downfield shifts of H-1', C-19 and C-4 signals from δ 4.84, 72.59 and 38.38 ppm in **2** to δ 6.29, 176.61 and 44.50 in **3**. These facts suggest that **3** is β-D-glucopyranosyl-*ent*-15,16-dihydroxypimar-8(14)-en-19-oiclate.

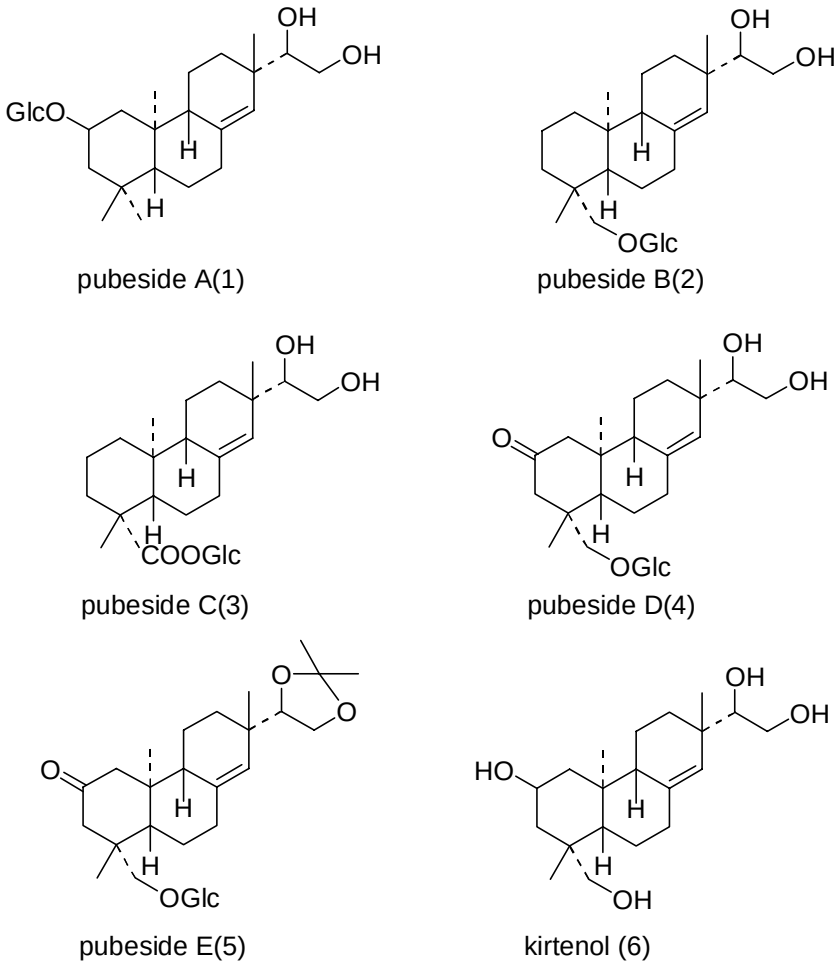
Pubeside D (**4**), $C_{26}H_{42}O_9$ M 498, mp. 250~253°C. The differences of the ^1H and ^{13}C NMR spectra between **1** and **4** are that those of **4** lack 2-CHOH signal, and the down-field shifts of C-1, C-2 and C-3 signals from δ 48.08, 72.87 and 46.90 ppm in **1** to δ 53.84, 212.19 and 50.89 in **4**. These facts suggest that **2** is 2-oxo-19-β-D-glucosylkire-nol, namely *ent*-2-oxo-15,16,19-trihydroxypimar-8(14)-en-19-O-β-D-glucopyranoside.

Pubeside E (**5**), $C_{29}H_{46}O_9$ M 538, mp. 240~243°C. The comparison of ^1H and ^{13}C NMR spectra of **4** with those of **5** showed the presence of the extra CMe_2 signals [δ 1.48, 1.41 (each 3H, s), 108.70 (s), 26.65 (q) and 25.51 (q)] in **5** and downfield shift of C-15 and C-16 signals from δ 76.81 and 63.98 ppm in **4** to δ 80.66 and 65.67 in **5**. These facts suggest that **5** is acetonide of **4**, namely *ent*-2-oxo-15, 16,19-trihydroxypimar-8(14)-en-19-O-β-D-glucopyranoside-15,16-acetonide.

Table 1 ^{13}C NMR data of pubesides A~E and kirenol in C_5D_5N (100.6MHz, δ in ppm)

C	**1**	**2**	**3**	**4**	**5**	**6**
1	48.08 t	39.22 t	39.48 t	53.84 t	53.85 t	49.50 t
2	72.87 d	19.08 t	20.19 t	212.19 s	212.02 s	64.05 d
3	46.90 t	36.81 t	38.64 t	50.89 t	50.89 t	45.82 t
4	34.78 s	38.38 s	44.50 s	43.67 s	43.57 s	41.08 s
5	54.62 d	56.09 d	56.67 d	54.86 d	54.79 d	55.71 d
6	22.63 t	22.89 t	24.58 t	22.90 t	22.94 t	22.78 t
7	36.34 t	36.43 t	37.18 t	36.20 t	36.25 t	36.93 t
8	138.10 s	138.33 s	138.42 s	137.15 s	138.74 s	138.18 s
9	51.23 d	51.12 d	50.57 d	50.75 d	50.06 d	51.48 d
10	39.86 s	38.42 s	39.29 s	43.67 s	43.88 s	39.90 s
11	18.97 t	18.90 t	18.95 t	18.94 t	18.69 t	19.20 t
12	32.93 t	32.94 t	33.04 t	32.56 t	31.88 t	32.94 t
13	38.09 s	37.97 s	38.05 s	38.06 s	36.25 s	38.10 s
14	129.98 d	129.49 d	129.17 d	130.54 d	128.05 d	129.94 d
15	76.80 d	76.76 d	76.68 d	76.81 d	80.66 d	76.77 d
16	64.12 t	64.03 t	63.91 t	63.98 t	65.67 t	64.08 t
17	23.41 q	23.32 q	23.45 q	23.24 q	23.07 q	23.40 q
18	33.96 q	28.13 q	29.07 q	28.22 q	28.22 q	28.40 q
19	23.06 q	72.59 t	176.61 s	73.73 t	73.77 t	64.99 t
20	15.65 q	16.05 q	14.29 q	15.98 q	16.26 q	17.10 q
Glc-1	102.97 d	105.58 d	95.80 d	105.55 d	105.52 s	
Glc-2	75.44 d	75.42 d	74.05 d	75.30 d	75.30 d	
Glc-3	78.42 d	78.51 d	79.16 d	78.38 d	78.40 d	
Glc-4	71.88 d	71.89 d	71.10 d	71.83 d	71.84 d	
Glc-5	78.76 d	78.78 d	79.39 d	78.51 d	78.51 d	
Glc-6	62.97 t	62.97 t	62.23 t	63.06 t	63.07 t	
$>CMe_2$ of acetonide					108.70 s 26.65 q 25.51 q	

Figure 1 New Diterpenoid Glucosides from *Siegesbeckia pubescens*



Above-mentioned conclusions were further supported by ^{1}H-^{1}H, ^{1}H-^{13}C, COLOC, EIMS, negative FABMS spectra of pubesides A~E and the spectral data of their full acetates (hexaacetates of pubeside A~D and tetraacetate of pubeside E and kirenol).

Acknowledgment

Project was supported by the Applied Basic Research Foundation of Yunnan Province (97C089M).

References and Notes

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Pubeside A (**1**), $C_{26}H_{44}O_8$ MW 484, mp. 265~267°C, 40 mg, $[\alpha]_D^{26}$ -36.78 (MeOH, c 0.2477); IR ν KBr cm^{-1}: 3400, 1703, 1650, 1455, 1365, 1075, 1035, 1015; EIMS(20eV) *m/z*(%): 448$[M-2H_2O]^+$(32), 423$[M-CHOHCH_2OH]^+$(5), 422(6), 407(1), 389(0.5), 369(22), 322(1), 304(2), 286(18), 271(14), 268(16), 253(19), 243(95), 227(9), 185(50), 135(70), 121(78), 107(63), 95(52), 81(93), 73(72), 69(92), 60(80), 43(100); ^{1}H NMR(400MHz, C_5D_5N δppm, JHz): 5.42(1H, br s, 14-H), 5.06(1H, d, 7.8Hz, 1'-H), 4.57(1H, dd, 11.8, 2.2Hz, 6'-Ha), 4.42(1H, dd, 11.8, 5.3 Hz, 6'-Hb), 4.36(1H, t, 8.8Hz, 3'-H), 4.36(1H, t, 8.8Hz, 4'-H), 4.28(1H, dd, 9.7, 3.2 Hz, 2α - H), 4.18(1H, dd, 12.1, 7.2 Hz, 16-Ha), 4.06(4H, m, 2'-H, 5'-H, 15-H, 16-Hb), 1.16(3H, s, 17-Me), 0.83(3H, s, 20-Me), 0.77(3H, s, 18-Me), 0.63(3H, s, 19-Me). Pubeside B (**2**), $C_{26}H_{44}O_8$ MW 484, mp. 257~260°C, 75mg, $[\alpha]_D^{25}$ -67.01 (MeOH, c 0.237); IR ν KBr cm^{-1}: 3400, 1705, 1650, 1450, 1380, 1365, 1075, 1030, 880, 850; FAB$^-$MS *m/z*(%): 483$[M-1]^-$(100), 159(6), 101(15); ^{1}H NMR(400MHz, C_5D_5N δppm, JHz): 5.37(1H, br s, 14-H), 4.84(1H, d, 7.7Hz, 1'-H), 4.59(1H, dd, 11.5, 2.2Hz, 6'-Ha), 4.41(1H, dd, 11.5, 5.3 Hz, 6'-Hb), 4.38, 3.44(each 1H, ABd, 9.5Hz, 19-H_2), 4.25(2H, m, 4'-H, 5'-H), 4.18(1H, dd, 12.1, 8.4 Hz, 16-Ha), 4.02(4H, m, 2'-H, 3'-H, 15-H, 16-Hb), 1.20(3H, s, 18-Me), 1.16(3H, s, 17-Me), 0.57(3H, s, 20-Me). Pubeside C (**3**), $C_{26}H_{42}O_9$ MW 498, mp. 261~263°C, 100 mg, $[\alpha]_D^{26}$ -9.6 (MeOH, c 0.626); IR ν KBr cm^{-1}: 3400, 1732, 1720, 1640, 1450, 1380, 1360, 1228, 1075, 1025, 880, 850; FAB$^-$MS *m/z*(%): 497$[M-1]^-$(12), 335(100), 159(2), 119(4); ^{1}H NMR(400MHz, C_5D_5N δppm, JHz): 6.29(1H, d, 8.1Hz, 1'-H), 5.40(1H, br s, 14-H), 4.39(2H, m, 6'-H_2), 4.35(1H, t, 9.0Hz, 4'-H), 4.25(1H, t, 8.9Hz, 3'-H), 4.16(1H, t, 8.5Hz, 2'-H), 4.06(2H, m, 16-H_2), 4.03(2H, m, 5'-H, 15-H), 1.29(3H, s, 18-Me), 1.18(3H, s, 17-Me), 0.89(3H, s, 20-Me). Pubeside D (**4**), $C_{26}H_{42}O_9$ MW 498, mp. 250~253°C, 76 mg, IR ν KBr cm^{-1}: 3400, 1732, 1720, 1640, 1450, 1380, 1360, 1228, 1075, 1025, 880, 850; FAB$^-$MS *m/z*(%): 497$[M-1]^-$(100), 159(8), 119(29), 101(10); ^{1}H NMR(400MHz, C_5D_5N δppm, JHz): 5.43(1H, br s, 14-H), 4.71(1H, d, 7.7Hz, 1'-H), 4.56(1H, dd, 11.8, 2.2Hz, 6'-Ha), 4.34(1H, dd, 11.8, 5.8 Hz, 6'-Hb), 4.05, 3.37(each 1H, ABd, 10.1Hz, 19-H_2), 4.18(3H, m, 3'-H, 4'-H, 16-Ha), 3.97(4H, m, 2'-H, 5'-H, 15-H, 16-Hb), 2.87, 2.19(each 1H, d, 12.4Hz, 3-H_2), 2.28, 2.19(each 1H, d, 13.4Hz, 1-H_2), 1.14(6H, s, 17-Me, 18-Me), 0.68(3H, s, 20-Me). Pubeside E (**5**), $C_{29}H_{46}O_9$ MW 538, mp. 240~243°C, 50 mg, IR ν KBr cm^{-1}: 3400, 3310, 1684, 1650, 1425, 1370, 1365, 1288, 1085, 1058, 863; FAB$^-$MS *m/z*(%): 537$[M-1]^-$(100), 159(17), 119(49), 101(14); ^{1}H NMR(400MHz, C_5D_5N δppm, JHz): 5.27(1H, br s, 14-H), 4.73(1H, d, 7.7Hz, 1'-H), 4.57(1H, dd, 10.9, 2.2Hz, 6'-Ha), 4.35(1H, dd, 10.9, 5.8 Hz, 6'-Hb), 4.21(1H, t, 8.7Hz, 3'-H), 4.16(1H, t, 9.0Hz, 4'-H), 4.10, 3.41(each 1H, ABd, 10.1Hz, 19-H_2), 4.08(1H, m, 15-H), 3.97(3H, m, 2'-H, 5'-H, 16-Ha), 3.85(1H, m, 16-Hb), 2.89, 2.20(each 1H, d, 13.0Hz, 3-H_2), 2.40, 2.22(each 1H, d, 12.8Hz, 1-H_2), 1.48, 1.41(each 3H, s, >CMe_2 of acetonide), 1.15(6H, s, 18-Me), 1.01(6H, s, 17-Me), 0.81(3H, s, 20-Me).

Received May 15, 2000