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SESQUITERPENOIDS FROM *Petasites tatewakianus*

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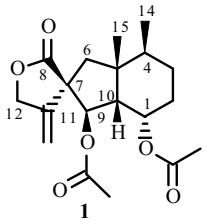
The genus *Petasites* (Asteraceae) comprises approximately 15 species, most of which are perennial herbs with creeping underground rhizomes and large leaves during the growing season [1]. Among the plants of this genus, the flower buds of *P. japonicus* are used as a remedy for headache, inflammation, and cough [2]. *Petasites tatewakianus* Kitam. is distributed mainly in the mountainous regions of northeast China, the Korean Peninsula, Japan, and the Far East region of Russia and Sakhalin Island. This plant has been cultivated in recent years due to its edible leafstalk as popular vegetable. As part of phytochemical researches of Asteraceae plants scattered in northeast China, we investigated the constitutes of the rhizomes of *Petasites tatewakianus* collected in Daxing′anling Mountains. Recently, two bakkenolides isolated from this plant were reported by our research group [3]. Subsequent investigation of this plant resulted in the isolation of six sesquiterpenoids with multiplicate skeletons.

Air-dried, ground rhizomes of *P. tatewakianus* (12.6 kg) were extracted with MeOH (7 days × 3) at room temperature to yield 526 g crude extract after evaporation of the solvent *in vacuo*. The crude extract was suspended in water and successively partitioned with *n*-hexane and $CHCl_3$. The $CHCl_3$ soluble fraction (196 g) was subjected to silica gel column chromatography (CC) with *n*-hexane–acetone gradient elucidation. After repeated silica gel CC, low-pressure C-18 silica gel CC purification, and recrystallization, six sesquiterpenoids were obtained. When the spectroscopic data (EI-MS, ^{1}H NMR, and ^{13}C NMR) were compared with those reported in the literature, the isolates were identified respectively as bakkenolide-L (**1**) [4], petasipaline B (**2**) [5], oplopanone (**3**) [6], pulioplopanone B (**4**) [7], 8β-hydroxyeremophil-7(11)-en-12,8-olide (**5**) [8], and oplodiol (**6**) [9]. All the compounds were isolated from *P. tatewakianus* for the first time. This is the second report of bakkenolide **1** from a natural source previously isolated from the root of *Petasites formosanus* [4]. Herein we reported its ^{13}C NMR data for the first time. Compound **6** is the first eudesmane-type sesquiterpenoid isolated from *Petasites* species, which is reasonable in the biogenetic pathway in that eudesmane is considered the biosynthetic precursor of eremophilane and bakkane sesquiterpenes [10].

Bakkenolide-L (1): colorless needles, $C_{19}H_{26}O_6$; EI-MS, (I_{rel}, %) *m/z*: 350 $[M]^+$ (1), 308 (2), 248 (5), 230 (2), 186 (5), 149 (2), 138 (7), 111 (12), 109 (17), 43 (100). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz, TMS): 5.71 (1H, d, J = 11.5, H-9), 5.13 (2H, dt, J = 1.5, 16.0, H-13), 4.60, 4.64 (each 1H, dt, J = 2.0, 13.0, H-12), 4.99 (1H, dt, J = 5.0, 12.0, H-1), 1.88 (3H, s, OAc), 1.86 (3H, s, OAc), 1.03 (3H, s, H-15), 0.83 (3H, s, H-14). ^{13}C NMR (125 MHz, $CDCl_3$, δ, TMS): 69.8 (C-1), 25.6 (C-2), 28.5 (C-3), 34.4 (C-4), 42.2 (C-5), 44.9 (C-6), 53.7 (C-7), 176.8 (C-8), 79.8 (C-9), 50.79 (C-10), 146.6 (C-11), 69.6 (C-12), 107.3 (C-13), 14.5 (C-14), 18.6 (C-15), 168.9 (OAc), 168.7 (OAc), 20.2 (OAc), 20.1 (OAc).



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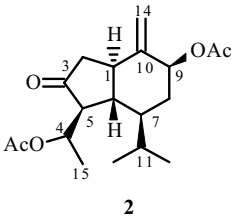

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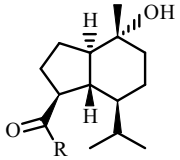
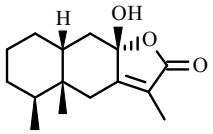


3, 4

3: R = CH_3; **4:** R = CH_2OH



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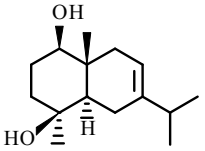

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Petasipaline B (2): colorless oil, $C_{19}H_{28}O_5$; EI-MS, (I_{rel}, %) *m/z*: 336 $[M]^+$ (1), 276 (3), 234 (32), 216 (9), 201 (2), 173 (12), 159 (3), 145 (8), 131 (5), 110 (7), 43 (100). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz, TMS): 5.47 (1H, t, J = 3.0, H-9), 5.02 (1H, dq, J = 7.0, 3.0, H-4), 5.04, 4.72 (each 1H, d, J = 1.5, H-14), 2.04 (3H, s, OAc), 2.03 (3H, s, OAc), 1.15 (3H, d, J = 7.0, H-15), 0.91 (3H, d, J = 7.0, H-13), 0.70 (3H, d, J = 7.0, H-12). ^{13}C NMR (125 MHz, $CDCl_3$, δ, TMS): 42.2 (C-1), 42.5 (C-2), 214.7 (C-3), 69.5 (C-4), 57.2 (C-5), 49.0 (C-6), 43.8 (C-7), 31.1 (C-8), 73.9 (C-9), 145.7 (C-10), 27.5 (C-11), 21.6 (C-12), 15.4 (C-13), 110.4 (C-14), 15.2 (C-15), 170.9 (OAc), 170.1 (OAc), 21.6 (OAc), 21.4 (OAc).

Oplopanone (3): colorless oil, $C_{15}H_{26}O_2$; EI-MS, (I_{rel}, %) *m/z*: 238 $[M]^+$ (4), 177 (2), 153 (40), 135 (27), 111 (7), 71 (15), 55 (8), 43 (100). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz, TMS): 2.18 (3H, s, H-15), 1.19 (3H, s, H-14), 0.89 (3H, d, J = 6.9, H-12), 0.69 (3H, d, J = 6.9, H-13). ^{13}C NMR (125 MHz, $CDCl_3$, δ, TMS): 54.7 (C-1), 24.2 (C-2), 27.0 (C-3), 210.4 (C-4), 56.0 (C-5), 48.4 (C-6), 45.7 (C-7), 22.0 (C-8), 41.0 (C-9), 72.0 (C-10), 28.5 (C-11), 22.0 (C-12), 14.5 (C-13), 19.3 (C-14), 20.9 (C-15).

Pulioplopanone B (4): colorless oil, $C_{15}H_{26}O_3$; EI-MS, *m/z* (I_{rel}, %): 254 $[M]^+$ (2), 223 (27), 177 (20), 109 (13), 81 (29), 69 (36), 55 (63), 43 (100). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz, TMS): 4.27 (1H, dd, J = 19.1, 4.7, H-15), 4.22 (1H, dd, J = 19.1, 4.4, H-15), 3.09 (1H, dd, J = 4.7, 4.4, OH-15), 1.21 (3H, s, H-14), 0.82 (3H, d, J = 6.9, H-12), 0.58 (3H, d, J = 6.9, H-13). ^{13}C NMR (125 MHz, $CDCl_3$, δ, TMS): 55.8 (C-1), 24.3 (C-2), 28.4 (C-3), 211.3 (C-4), 49.30 (C-5), 45.9 (C-6), 48.1 (C-7), 21.7 (C-8), 40.9 (C-9), 71.9 (C-10), 28.9 (C-11), 21.7 (C-12), 14.3 (C-13), 19.3 (C-14), 67.0 (C-15).

8*β*-Hydroxyeremophil-7(11)-en-12,8-olide (5): colorless needles, $C_{15}H_{22}O_3$; EI-MS, *m/z* (I_{rel}, %): 250 $[M]^+$ (7), 232 (7), 222 (25), 126 (18), 109 (100), 91 (19), 79 (18), 67 (31), 55 (50), 53 (52), 41 (81). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz, TMS): 1.72 (3H, s, H-13), 0.98 (3H, s, H-15), 0.72 (3H, d, J = 5.2, H-14). ^{13}C NMR (125 MHz, $CDCl_3$, δ, TMS): 26.1 (C-1), 20.5 (C-2), 30.5 (C-3), 29.6 (C-4), 40.3 (C-5), 35.0 (C-6), 159.3 (C-7), 104.1 (C-8), 38.9 (C-9), 39.5 (C-10), 122.4 (C-11), 172.8 (C-12), 8.2 (C-13), 21.4 (C-14), 16.0 (C-15).

Oplodiol (6): colorless needles, $C_{15}H_{26}O_2$; EI-MS, *m/z* (I_{rel}, %): 238 $[M]^+$ (7), 220 (19), 202 (7), 187 (38), 161 (36), 159 (67), 147 (10), 145 (16), 119 (38), 107 (19), 93 (44), 43 (100). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz, TMS): 5.27 (1H, ddd, J = 1.0, 2.5, 4.0, H-8), 3.23 (1H, dd, J = 4.0, 11.5, H-1), 1.11 (3H, s, H-14), 0.96 (3H, d, J = 6.5, H-12), 0.95 (3H, d, J = 6.5, H-13), 0.89 (3H, s, H-15). ^{13}C NMR (125 MHz, $CDCl_3$, δ, TMS): 79.9 (C-1), 40.7 (C-2), 39.4 (C-3), 71.0 (C-4), 46.2 (C-5), 26.7 (C-6), 141.9 (C-7), 116.1 (C-8), 23.0 (C-9), 37.6 (C-10), 35.0 (C-11), 21.8 (C-12), 21.2 (C-13), 29.9 (C-14), 11.7 (C-15).

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REFERENCES

1. Y. Jiang and B. T. Li, *Flora Republicae Popularis Sinicae*, Institutum Academiae Sience Press, Beijing, 1999, Vol. **77** (1), p. 94.
2. Jiangsu New Medical College, *Chinese Medicine Dictionary*, Shanghai People′s Publishing House, Shanghai, 1977, p. 2483.
3. X. W. Dong, R. J. Li, X. Gao, and K. H. Row, *Fitoterapia*, **81**, 153 (2010).
4. T. S. Wu, M. S. Kao, P. L. Wu, F. W. Lin, L. S. Shi, M. J. Liou, and C. Y. Li, *Chem. Pharm. Bull*., **47**, 375 (1999).
5. K. Hayashi, *Phytochemistry*, **28**, 3373 (1989).
6. A. S. Feliciano, M. Medarde, M. Gordaliza, and M. J. Lucas, *J. Nat. Prod*., **58**, 1059 (1995).
7. J. Triana, M. Lopez, F. J. Perez, J. Gonzalez-Platas, J. Quintana, F. Estevez, F. Leon, and J. Bermejo, *J. Nat. Prod*., **68**, 523 (2005).
8. A. M. Tan, H. Yang, Y. S. Li, Z. M. Bi, M. Zhang, and Z. T. Wang, *Chin. Pharm. J*., **39**, 498 (2004).
9. A. S. Feliciano, M. Medarde, M. Gordaliza, E. D. Olmo, and J. M. M. D. Corral, *Phytochemistry*, **28**, 2717 (1989).
10. J. Porter and S. L. Spurgeon, *Biosynthesis of Isoprenoid Compounds*, John Wiley & Sons, Vol. **1**, 1981.