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SESQUITERPENOIDS FROM *Aster himalaicus*

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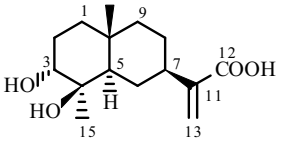
Aster himalaicus, a perennial plant, grows only in the Himalayas at high altitudes (3600–4800 m), such as in Nepal, Sikkim, Bhutan, Burma, Tibet, and Yunnan Province of China. The aerial parts of this plant have been extensively used as folk medicine in Tibet for treatment of coughs, bronchitis, hepatitis, snakebite, and so on [1]. Several flavonoids isotated from *Aster himalaicus* were reported recently [2]. For the purpose of searching for antibacterial sesquiterpenoids, we investigated the chemical constituents of this plant collected in the marginal areas of Qinghai-Tibet Plateau in China. Recently, we reported a new and several known eudesmane sesquiterpenoid [3]. To the best of our knowledge, there have been only one eudesmane sesquiterpene, 6α-methoxy-4(15)-eudesmen-1β-ol, obtained from *Aster* species before our research [4]. Subsequent investigation of this plant resulted in the isolation of four eudesmane sesquiterpenoids, of which compounds **2–4** previously yielded their ester form. Herein we report their NMR and MS data for the first time.

The whole plants of *Aster himalaicus* were collected from Huzhu County, Qinghai Province, P. R. China in September 2006, and was identified by Assoc. Prof. Hong Zhao, Marine College, Shandong University at Weihai. The powdered air-dried plants of *Aster himalaicus* (9.8 kg) were extracted with petroleum ether–Et_2O–MeOH (1:1:1) three times (7 days each time) at room temperature. The extract was evaporated under vacuum to afford a residue (350 g), which was purified by a series of column chromatographic (CC) procedures, such as silica gel CC and low pressure C-18 CC, to afford four eudesmane sesquiterpenoids **1–4**.

3β-Hydroxy-*epi*-ilicic acid (1): colorless needles, mp 181–183°C, EI-MS (I_{rel}, %): 268 (4) $[M]^+$, 253 (1) $[M - Me]^+$, 250 (2) $[M - H_2O]^+$, 232 (3) $[M - 2H_2O]^+$, 209 (2), 191 (2), 149 (5), 78 (65), 63 (100); For ^1H NMR data, see Table 1. ^{13}C NMR (100 MHz, $CDCl_3$, δ): 35.9 (C-1), 26.4 (C-2), 75.0 (C-3), 74.0 (C-4), 46.8 (C-5), 27.2 (C-6), 41.6 (C-7), 29.3 (C-8), 44.7 (C-9), 34.5 (C-10), 147.7 (C-11), 168.7 (C-12), 122.4 (C-13), 19.0 (C-14), 26.3 (C-15) [5, 6].

3α-Hydroxycostic acid (2): colorless needles, mp 174–176°C, EI-MS (I_{rel}, %): 250 (15) $[M]^+$, 235 (3) $[M - Me]^+$, 232 (4) $[M - H_2O]^+$, 149 (18), 99 (35), 69 (55). 57 (92), 43 (100). For ^1H NMR data, see Table 1. ^{13}C NMR (100 MHz, $CDCl_3$, δ): 39.0 (C-1), 33.2 (C-2), 73.8 (C-3), 153.5 (C-4), 42.9 (C-5), 26.2 (C-6), 40.5 (C-7), 31.7 (C-8), 34.7 (C-9), 38.7 (C-10), 146.5 (C-11), 171.5 (C-12), 121.7 (C-13), 21.8 (C-14), 106.9 (C-15) [7, 8].

5α-Hydroxycostic acid (3): colorless needles, mp 93–95°C, EI-MS (I_{rel}, %): 250 (2) $[M]^+$, 235 (6) $[M - Me]^+$, 232 (6) $[M - H_2O]^+$, 217 (3), 204 (3), 137 (12), 96 (10), 41 (100). For ^1H NMR data, see Table 1. ^{13}C NMR (100 MHz, $CDCl_3$, δ): 36.0 (C-1), 26.1 (C-2), 34.2 (C-3), 151.8 (C-4), 75.4 (C-5), 31.6 (C-6), 30.9 (C-7), 22.2 (C-8), 34.8 (C-9), 37.8 (C-10), 145.5 (C-11), 171.5 (C-12), 124.8 (C-13), 19.2 (C-14), 107.6 (C-15) [9].



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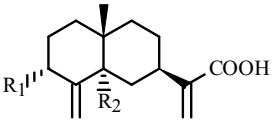

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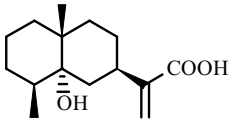

4

2: R_1 = OH, R_2 = H
3: R_1 = H, R_2 = OH

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TABLE 1. ^{1}H NMR Chemical Shifts of **1–4** (400 MHz, $CDCl_3$, δ, ppm, J/Hz)

C atom	1	2	3	4
1α	1.07 m	1.83 m	1.03 m	1.13 m
1β	1.25 (br.d, J = 12.8)	1.72 m	1.59 m	1.59 m
2α	1.63 m	1.90 m	1.18 m	1.23 m
2β	2.20 m	1.58 m	1.50 m	1.36 m
3α	–	–	2.58 (dtt, J = 12.0, 5.0, 1.5)	2.05 (ddd, J = 12.0, 12.0, 5.0)
3β	3.47 (t, J = 3.4)	4.42 (dd, J = 4.8, 1.2)	2.05 (br.ddd, J = 12.0, 3.0, 3.0)	1.34 (br.d, J = 12.0)
4α	–	–	–	1.58 (dq, J = 7.0, 5.0)
5	1.52 (dd, J = 12.8, 4.4)	1.97 (dd, J = 9.6, 4.4)	–	–
6α	1.57 m	1.66 m	1.81 m	1.20 (dd, J = 12.5, 4.0)
6β	1.30 m	1.50 m	1.58 m	1.86 (dd, J = 12.5,12.5)
7	2.50 (dddd, J = 12.8, 12.8, 4.4, 4.4)	2.48 (ddddd, J = 12.0, 12.0, 3.5, 3.5, 1.0)	3.02 (br.ddddd, J = 12.0, 12.0, 3.0, 3.0, 1.0)	3.06 (ddddd, J = 12.5, 12.5, 4.0, 4.0,1.0)
8α	1.69 m	1.60 m	1.60 m	1.63 m
8β	1.45 m	1.40 m	1.58 m	1.53 m
9α	1.33 m	1.55 m	1.36 m	1.57 m
9β	1.55 m	1.18 m	1.29 m	1.50 m
13a	6.14 br.s	6.18 br.s	6.25 br.s	6.24 br.s
13b	5.62 br.s	5.65 br.s	5.61 br.s	5.63 br.s
14	1.10 s	1.10 br.s	0.94 s	1.08 s
15	1.18 s	5.45, 5.43 br.s	4.73, 4.57 br.s	0.90 s

5α-Hydroxy-4α,15-dihydrocostic acid (4): colorless needles, mp 83–85°C, EI-MS (I_{rel}, %): 252 (3) $[M]^+$, 237 (3) $[M - Me]^+$, 234 (5) $[M - H_2O]^+$, 219 (8), 182 (18), 55 (74), 41 (100). For ^{1}H NMR data, see Table 1. ^{13}C NMR (100 MHz, $CDCl_3$, δ): 38.1 (C-1), 26.3 (C-2), 34.4 (C-3), 41.2 (C-4), 75.7 (C-5), 28.0 (C-6), 34.8 (C-7), 17.0 (C-8), 37.9 (C-9), 36.6 (C-10), 145.1 (C-11), 171.5 (C-12), 125.2 (C-13), 16.7 (C-14), 22.2 (C-15) [9].

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