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SESQUITERPENES AND TRITERPENES FROM *Aeschynanthus mengxinggensis*

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The genus *Aeschynanthus* is a member of the family Gesneriaceae, subfamily Cyrtandroideae, tribe Trichosporeae and is a large genus of Old World tropical herbs native primarily to Southeast Asia. There are about 185 species distributed in southern and southeastern Asia, the islands of Indonesia, New Guinea, and the Philippines [1].

Flavonoids and phenylpropanoids were the main compound isolated from the family Gesneriaceae [2–5] in early phytochemical research. 3-Desoxyanthocyanins, as evidenced by chemotaxonomy, was only isolated from the subfamily Gesneriodeae of the Gesneriaceae and was used to divide Gesneriaceae into the subfamilies Gesneriodeae and Cyrtandroideae [1, 2]. However, terpenoids are rarely found in the family Gesneriaceae, and about 20 triterpenoids have been isolated from *Paradrymonia macrophylla* [6], *Conandron ramondioides* [7], *Chirtia longgangensis* [8], *Chirita eburnea* [9], *Aeschynanthus bracteatus* [10], and *A. mengxinggensis* [11]. The type of triterpenoids from Gesneriaceae was mainly Δ^{12}-oleanene and Δ^{12}-ursene [6–8, 10]; in particular, the positions of C-2 and C-3 were replaced by the hydroxyl group [6, 10, 11]. Only one triterpene, of the type of cycloartane, cycloart-23-ene-3β,25-diol, was isolated from *Chirita eburnea* [9]. Two monoterpenoids and a sesquiterpene were isolated from *A. bracteatus* [10]. Except terpenoids from *P. macrophylla*, other terpenoids were isolated from Cyrtandroideae. In our previous studies on this species, isolation of three triterpenes was reported [11].

In the present study, *A. mengxinggensis* growing in Xishuangbanna of Yunnan Province was analyzed. A sample of the leaves of *A. mengxinggensis* was collected in May 2005, and a voucher specimen was kept at the herbarium of the Institute of Natural Products, Henan University.

Dried leaves of *A. mengxinggensis* (700 g) were extracted with ethanol (95%) at room temperature. After evaporation of the ethanol, the residue was suspended in water and extracted with ethyl acetate and then with butan-1-ol. The ethyl acetate extract (5.6 g) was subjected to silica gel (200–300 mesh, Qingdao Marine Chemical Inc, China) column chromatography and elution with chloroform–acetone mixtures (95:5 to 9:1). Terpenoids were found in the chloroform–acetone (20:1 to 10:1) fractions. All fractions were combined to obtain 980 mg and repeatedly subjected to column chromatography on silica gel (10–40 μm, Qingdao Marine Chemical Inc, China) and elution with chloroform–acetone (10:1) and Sephadex LH-20 column chromatography using acetone as elution to afford compounds **1–6**.

These compounds were identified using MS and NMR spectrum and have been isolated from the family Gesneriaceae for the first time.

4(15),11-Eudesmadiene-1β-ol (1), $C_{15}H_{24}O$, oil. EI-MS *m/z*: 220, 203, 187, 159, 107, 93. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 4.83 (1H, br.s, H-12a), 4.81 (1H, br.s, H-12b), 4.77 (1H, br.s, H-15a), 4.54 (1H, br.s, H-15b), 3.09 (1H, dd, J = 11.4, 4.7, H-1α), 2.16 (1H, dddd, J = 13.4, 5.0, 2.3, H-3β), 1.92 (2H, m, H-3α, 9β), 1.81 (1H, tt, J = 11.0, 4.0, H-7α), 1.68 (3H, br.s, CH_3-13), 1.60 (2H, m, H-8β, 2β), 1.55 (2H, m, H-5α, 6β), 1.48 (1H, m, H-2α), 1.32 (2H, m, H-8α, 6α), 0.95 (1H, m, H-9α), 0.68 (3H, s, CH_3-14). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 79.3 (C-1), 31.5 (C-2), 34.2 (C-3), 148.7 (C-4), 47.6 (C-5), 26.5 (C-6), 45.3 (C-7), 28.9 (C-8), 37.0 (C-9), 40.2 (C-10), 150.3 (C-11), 108.3 (C-12), 20.9 (C-13), 10.2 (C-14), 106.8 (C-15) according to previously published spectral data [12].

11-Eudesmene-1β,4α-diol (2), $C_{15}H_{26}O_2$, oil. EI-MS *m/z*: 238, 223, 220, 213, 195, 177, 159, 135, 123. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 4.72 (2H, m, H-12), 3.32 (1H, dd, J = 4.4, 11.2, H-1), 1.94 (1H, m, H-7),1.90 (1H, ddd, J = 3.5, 3.5, 13.5, H-9β), 1.84 (1H, m, H-6α), 1.79 (1H, ddd, J = 3.0, 3.5, 12.0, H-3β),1.75 (3H, s, CH_3-14), 1.72 (1H, m, H-2α),

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1.62 (1H, m, H-2β), 1.61 (1H, m, H-8α), 1.52 (1H, ddd, J = 3.5, 12.0, 13.5, H-3α), 1.38 (1H, dddd, J = 3.50, 13.0, 13.5, 17.0, H-8β), 1.28 (1H, m, H-5), 1.26 (1H, m, H-6β), 1.13 (1H, ddd, J = 4.0, 13.0, 13.5, H-9α), 1.11 (3H, s, CH_3-15), 0.89 (3H, s, CH_3-13). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 79.2 (C-1), 28.5 (C-2), 40.8 (C-3), 71.6 (C-4), 52.6 (C-5), 25.7 (C-6), 45.4 (C-7), 267.6 (C-8), 40.5 (C-9), 38.8 (C-10), 150.4 (C-11), 108.3 (C-12), 21.1 (C-13), 13.0 (C-14), 22.6 (C-15) according to previously published spectral data [13].

1β,4β,7α-Eudesmanetriol (3), $C_{15}H_{28}O_3$, mp 135–137°C. EI-MS *m/z*: 256, 238, 223, 220, 213, 195, 177, 159, 135, 123. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.21 (1H, dd, J = 12.4, H-1α), 1.10 (3H, s, H-15), 0.96 (3H, s, H-14), 0.94 (6H, d, J = 7, H-12, H-13). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 80.5 (C-1), 40.1 (C-2), 40.6 (C-3), 72.1 (C-4), 46.1 (C-5), 29.3 (C-6), 74.8 (C-7), 30.1 (C-8), 27.7 (C-9), 35.8 (C-10), 40.5 (C-11), 17.4 (C-12), 17.5 (C-13), 12.2 (C-14), 29.9 (C-15) according to previously published spectral data [14].

12-Ursene-2α,3β-diol (4), $C_{30}H_{50}O_2$. EI-MS *m/z*: 442, 427, 218, 204, 189, 177, 161, 147, 133, 121, 109. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 5.19 (1H, br.s, H-12), 3.70 (1H, ddd, J = 11.2, 9.6, 4.6, H-2), 3.01 (1H, d, J = 9.6, H-3), 0.67 (3H, s, H-23), 0.63 (3H, s, H-24), 0.84 (3H, s, H-25), 0.81 (3H, s, H-26), 0.81 (3H, s, H-26), 1.03 (3H, d, J = 5.9, H-29), 1.11 (3H, d, J = 6.1, H-30). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 38.4 (C-1), 68.7 (C-2), 83.1 (C-3), 38.4 (C-4), 55.2 (C-5), 18.3 (C-6), 32.4 (C-7), 39.9 (C-8), 47.7 (C-9), 36.9 (C-10), 23.4 (C-11), 124.0 (C-12), 139.3 (C-13), 42.0 (C-14), 28.7 (C-15), 26.8 (C-16), 33.6 (C-17), 58.9 (C-18), 39.6 (C-19), 39.6 (C-20), 31.2 (C-21), 41.6 (C-22), 28.1 (C-23), 16.0 (C-24), 16.0 (C-25), 16.9 (C-26), 23.3 (C-27), 28.4 (C-28), 17.4 (C-29), 21.3 (C-30) according to previously published spectral data [15].

3β,22α-Dihydroxy-23-oxo-12-oleanene-28,29-dioic acid (5), $C_{30}H_{44}O_7$, mp 224–225°C. EI-MS *m/z*: 516, 499, 487, 471, 443, 218, 204, 177, 161, 121. ^{1}H NMR (400 MHz, C_5D_5N, δ, ppm, J/Hz): 9.58 (1H, s, H-23), 5.70 (1H, br.s, H-12), 5.25 (1H, br.s, H-22), 4.08 (4H, t, J = 7.8, H-3), 1.34 (3H, s, H-24), 0.91 (3H, s, H-25), 1.01 (3H, s, H-26), 1.81 (3H, s, H-27), 1.73 (3H, s, H-30). ^{13}C NMR (100 MHz, C_5D_5N, δ, ppm): 38.7 (C-1), 27.2 (C-2), 71.7 (C-3), 56.4 (C-4), 47.9 (C-5), 21.3 (C-6), 31.4 (C-7), 40.4 (C-8), 47.3 (C-9), 36.1 (C-10), 23.4 (C-11), 122.8 (C-12), 144.3 (C-13), 42.0 (C-14), 32.7 (C-15), 36.8 (C-16), 49.0 (C-17), 40.9 (C-18), 42.2 (C-19), 42.8 (C-20), 31.9 (C-21), 74.6 (C-22), 207.1 (C-23), 9.7 (C-24), 16.0 (C-25), 17.9 (C-26), 27.3 (C-27), 180.4 (C-28), 181.8 (C-29), 21.3 (C-30) according to previously published spectral data [16].

2α,3β,23-Trihydroxy-12-oleanene-28-oic acid (6), $C_{30}H_{48}O_5$, mp 337–338°C. EI-MS *m/z*: 488, 471, 454, 443, 218, 204, 177, 161, 121. ^{1}H NMR (400 MHz, C_5D_5N, δ, ppm, J/Hz): 5.73 (1H, s, H-12), 3.57 (1H, d, J = 9.4, H-3), 3.49 (1H, m, H-2), 1.86 (3H, s, H-27), 1.72 (3H, s, H-24), 1.24 (3H, s, H-29), 1.15 (3H, s, H-25), 1.12 (3H, s, H-30), 1.10 (3H, s, H-26). ^{13}C NMR (100 MHz, C_5D_5N, δ, ppm): 47.1 (C-1), 68.9 (C-2), 78.7 (C-3), 43.4 (C-4), 48.4 (C-5), 18.6 (C-6), 33.1 (C-7), 40.1 (C-8), 48.5 (C-9), 38.5 (C-10), 23.8 (C-11), 123.5 (C-12), 144.1 (C-13), 42.4 (C-14), 28.3 (C-15), 23.8 (C-16), 47.0 (C-17), 43.59 (C-18), 46.2 (C-19), 30.8 (C-20), 34.2 (C-21), 33.0 (C-22), 67.1 (C-23), 14.0 (C-24), 17.6 (C-25), 17.2 (C-26), 26.1 (C-27), 178.4 (C-28), 32.8 (C-29), 23.7 (C-30) according to previously published spectral data [17].

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