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CHEMICAL CONSTITUENTS OF *Eria spicata*

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In order to know if *Eria* (Orchidaceae) plants can replace the precious medical *Dendrobium* (Orchidaceae) plants, chemical research was done on them. In this paper, we present the isolation and structures of eight compounds (**1–8**) from *Eria spicata* (D. Don) Hand.-Mazz. (*E. convallarioides*), which is distributed in Yunnan Province of China, Nepal, Sikkim, India, Burma, and Thailand [1]. The structures of the compounds were identified by a combination of spectroscopic methods (MS, ^{1}H, and ^{13}C NMR) and comparisons with the literature data as *N*-methyl hordenine (**1**) [2], *N*-oxide hordenine (**2**), 3-(4-hydroxy-3-methoxyphenyl)-propenal (**3**) [3], nudol (**4**) [4], erianol (**5**) [4], 5α,8α-epidioxy-(22*E*,24*R*)-ergosta-6,22-dien-3β-ol (**6**) [5], β-sitosterol (**7**), and daucosterol (**8**). Previous investigation on this plant has yielded erianol, nudol, erianthridin, and β-sitosterol [4]. Compounds **1**, **2**, **3**, **6**, and **8** were isolated from this plant for the first time.

The whole plant of *E. spicata* was collected from Lianghe, Yunnan Province of China in February 2006, and was identified by Prof. Hong Yu (Yunnan University).

The dried whole plant of *E. spicata* (1.9 kg) was extracted with 70% MeOH (four times, each 15 L for 7 days) at room temperature. After concentration of the combined extracts, the resulting gummy material was suspended in water and then partitioned with EtOAc to afford EtOAc and aqueous residues. The EtOAc residue (35 g) was subjected to column chromatography over silicon gel and eluted with petroleum ether–EtOAc (10:1) to (0:1) to give seven fractions.

Fraction 2 (1.54 g) was subjected to column chromatography on silica gel eluted with petroleum ether–EtOAc (15:1) and then on a silica gel column developed with petroleum ether–$CHCl_3$ (10:1) repeatedly to obtain **5** (16 mg). Compound **7** (900 mg) was obtained from fraction 3 (1.58 g) by recrystallization. Fraction 4 (3.5g) was purified on a SiO_2 column eluted with petroleum ether–$CHCl_3$ (from 6:1 to 3:1), and each subfraction was purified on a SiO_2 column eluted with petroleum ether–$CHCl_3$ (4:1) repeatedly to obtain **3** (40 mg), **4** (230 mg), and **6** (18 mg). Fraction 7 (12.1 g) was separated on silica gel eluted with $CHCl_3$–MeOH (from 15:1 to 5:1) and then isolated on Sephadex LH-20 (MeOH–$CHCl_3$ 1:1) to afford **8** (60 mg).

The aqueous residue was subjected to HPD-101 macroporous absorption resin eluted with H_2O, then with 95% ethanol. The H_2O portion (18.1g) was subjected to SiO_2 column chromatography eluted with $CHCl_3$–MeOH (from 5:1 to 0:1) to give four fractions. Fraction 2 (5.12 g) was purified on a SiO_2 column ($CHCl_3$–MeOH–H_2O 7:3:0.5) repeatedly to afford **2** (22 mg). Fraction 3 (3 g) was purified on SiO_2 column ($CHCl_3$–MeOH–H_2O 6.5:3.5:0.5) repeatedly to afford **1** (8 mg).

***N*-Methyl Hordenine (1)**. $C_{11}H_{18}NO$. ESI-MS 180 $[M]^+$. ^{1}H NMR (500 MHz, CD_3OD, δ, ppm, J/Hz): 7.15 (d, J = 8.5, H-2′, 6′), 6.74 (d, J = 8.5, H-3′, 5′), 3.51 (t, J = 8.5, H-1), 3.02 (t, J = 8.5, H-2), 3.19 (9H, s, $3CH_3$). ^{13}C NMR (125MHz, CD_3OD, δ): 157.8 (s, C-4′), 131.0 (d, C-2′, 6′), 127.3 (s, C-1′), 116.7 (d, C-3′, 5′), 68.8 (t, C-1), 29.5 (t, C-2), 53.7 (q, $3CH_3$).

***N*-Oxide Hordenine (2)**. $C_{10}H_{15}NO_2$. ESI-MS 181 $[M]^+$. ^{1}H NMR (500 MHz, CD_3OD, δ, ppm, J/Hz): 7.16 (d, J = 8.5, H-2′, 6′), 6.79 (d, J = 8.5, H-3′, 5′), 3.37 (6H, s, $2CH_3$), 3.34 (br.s, H-1), 3.02 (t, J = 8.5, H-2). ^{13}C NMR(125 MHz, CD_3OD, δ): 157.3 (s, C-4′), 130.6 (d, C-2′, 6′), 127.8 (s, C-1′), 116.5 (d, C-3′, 5′), 59.9 (t, C-1), 43.4 (q, $2CH_3$), 30.7 (t, C-2).

3-(4-Hydroxy-3-methoxyphenyl)-propenal (3). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 9.56 (1H, d, J = 7.8, H-1), 6.53 (1H, dd, J = 15.8, 7.8, H-2), 7.32 (1H, d, J = 15.8, H-3), 7.19 (1H, s, H-2′), 7.03 (1H, d, J = 8.2, H-6′), 6.88 (1H, d, J = 8.2, H-5′), 3.84 (3H, s, 3′-O$\underline{CH}_3$). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 153.0 (d, C-1), 114.9 (d, C-2), 193.5 (d, C-3), 126.6 (s, C-1′), 124.0 (d,C-2′), 146.9 (s, C-3′), 148.9 (s, C-4′), 109.4 (d, C-5′), 126.3 (d, C-6′), 55.9 (q, 3′-O$\underline{C}H_3$). EI-MS *m*/*z* (%): 178 $[M]^+$ (10), 149 (35), 85 (60), 71 (85), 57 (100).

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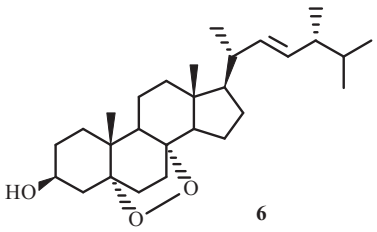

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Nudol (4). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 9.24 (1H, d, J = 9.0, H-5), 7.35 (2H, s, H-9, 10), 7.13 (1H, s, H-8), 7.12 (1H, d, J = 9.0, H-6), 7.03 (1H, s, H-1). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 109.2 (d, C-1), 148.0 (s, C-2), 141.9 (s, C-3), 151.5 (s, C-4), 129.7 (d, C-5), 116.9 (d, C-6), 154.5 (s, C-7), 112.0 (d, C-8), 127.3 (d, C-1), 126.6 (d, C-10), 133.9 (s, C-1′), 123.9 (s, C-2′), 118.9 (s, C-3′), 129.7 (s, C-4′), 60.1 (q, 3-OMe), 61.2 (4-OMe).

Erianol (5). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 36.9 (t, C-1), 30.9 (t, C-2), 76.2 (d, C-3), 40.3 (d, C-4), 46.7 (d, C-5), 26.6 (t, C-6), 117.5 (d, C-7), 139.1 (s, C-8), 49.6 (d, C-9), 34.8 (s, C-10), 21.4 (t, C-11), 39.3 (t, C-12), 43.3 (d, C-13), 54.9 (d, C-14), 22.9 (t, C-15), 27.9 (t, C-16), 55.9 (d, C-17), 11.8 (q, C-18), 14.1 (q, C-19), 36.3 (d, C-20), 18.9 (q, C-21), 30.4 (t, C-22), 37.0 (t, C-23), 38.7 (s, C-24), 152.4 (s, C-25), 109.3 (t, C-26), 19.4 (q, C-27), 15.1 (q, C-29), 27.5 (q, C-31), 27.2 (q, C-32).

5α,8α-Epidioxy-(22*E*,24*R*)-ergosta-6,22-dien-3β-ol (6). $C_{28}H_{44}O_3$. EI-MS: 428 $[M]^+$ (4), 410 $[M - H_2O]^+$ (5), 396 $[M - 32]^+$ (15), 251 (24), 152 (36), 81 (61), 69 (100). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 6.59 (d, J = 8.3, H-7), 6.50 (d, J = 8.3, H-8), 5.21 (d, J = 7.7, H-23), 5.16 (d, J = 7.7, H-24), 3.98 (m, H-3). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 34.6 (t, C-1), 30.0 (t, C-2), 66.4 (d, C-3), 36.9 (d, C-4), 82.1 (s, C-5), 135.4 (s, C-6), 130.7 (s, C-7), 79.7 (s, C-8), 51.1 (d, C-9), 36.9 (s, C-10), 23.4 (t, C-11), 39.3 (t, C-12), 44.5 (d, C-13), 51.6 (d, C-14), 19.9 (t, C-15), 28.6 (t, C-16), 56.3 (d, C-17), 12.8 (q, C-18), 18.1 (q, C-19), 39.7 (d, C-20), 20.8 (q, C-21), 135.2 (d, C-22), 132.3 (t, C-23), 42.7 (d, C-24), 20.6 (q, C-25), 33.0 (d, C-26), 19.6 (q, C-27), 17.5 (q, C-28).

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