1 Introduction

The genus Allophylus comprises about 255 species, 6 of which are distributed in China including 3 in Yunnan Province[1]. A. longipes has been historically used as a folk remedy in ‘Dai’ ethnopharmacy for the treatment of cold and inflammation, but its chemical constituents have not been investigated up to now. In the present phytochemical study on this species, twenty-five compounds were isolated and identified as cycloart-24-ene-3β, 26-dien-21-oic acid (2), zizyberenic acid (3), colubrinic acid (4), ent-4(15)-eudesmane-1β, 6α-diol (5), 4(15)-eudesmane-1β, 5α-diol (6), 4(15)-eudesmane-1β, 5α-diol (7), methyl asterate (8), betulin (9), betulonic aldehyde (10), betulnic acid (11), 3β-hydroxy-5α, 8α-epidioxyergosta-6,22-dien-28-oic acid (13), ursolic acid (14), scopoletin (15), fraxidin (16), cleomiscosin A (17), 4-hydroxy-3-methoxybenzaldehyde (18), 4-hydroxy-3-methoxyximacaldehyde (19), 2',6'-dihydroxy-4'-methoxyacetophenone (20), p-(aminoalkyl)-benzoic acid (21), 4-hydroxy-3-methoxybenzoic acid (22), 1-O-p-coumaroylgucose (23), β-sitosterol (24), and poriferast-5-ene-3β, 4β-diol (25). CONCLUSION: All the compounds were isolated from Allophylus longipes for the first time.

2 Apparatus and Reagents

NMR spectra were run on Bruker DRX-500 and AV-400 spectrometers with TMS as internal standard. Chemical shifts (δ) are expressed in ppm with reference to the solvent signals. Mass spectra were recorded on a VG Autospec-3000 spectrometer or an API QSTAR Pulsar 1 spectrometer. Column chromatography was performed on silica gel (48~75 μm, Qingdao Marine Chemical Co., Ltd., Qingdao, China), Rp-18 gel (20~45 μm, Fuji Silysia Chemical Ltd., Japan), and Sephadex LH-20 (Pharmacia Fine Chemical Co., Ltd., Sweden). Fractions were monitored by TLC (GF254, Qingdao Marine Chemical Co., Ltd., Qingdao, China), and spots were
was subjected to an Rp-18 column (MeOH-H2O, 20\% gel CC, Sephadex LH-20 CC (MeOH) and further
a CHCl3-Me2CO (1:0, 70:1, 50:1, 30:1, 20:1, 10:1, 5:1, 3:1, 2:1, 1:1, 1:2) to yield 6 fractions Fr. 1–6. Fraction 2 (15 g)
was chromatographed on silica gel (petroleum ether-EtOAc, 15:1 − 2:1) to give 1 (8 mg) and
4 (5 mg) while subfraction 2.3 (4 g) was subjected to silica gel
(petroleum ether- EtOAc, 20:1−1:2) to yield 2 (5 mg) and
5 (8 mg). Subfraction 2.4 (5 g) was subjected to an Rp-18 CC
(MeOH-H2O, 50%−95%) to give 19 (6 mg) and 20 (7 mg). Fraction 3 (9 g) was chromatographed on silica gel
(CDCl3-Me2CO, 25:1 − 1:1:2) to give 10 (1 012 mg), 25 (622 mg) and a mixture, which was chromatographed on
silica gel (petroleum ether- EtOAc, 15:1 − 1:2) to yield 21 (7 mg), 24 (6 mg). Fraction 4 (12 g) was subjected to an
Rp-18 CC (MeOH-H2O, 40%−95%) to give 26 (27 mg) and a mixture, which was chromatographed on silica gel
(petroleum ether- Me2CO, 25:1 − 1:2) to yield 13 (23 mg),
16 (31 mg) and 3 (71 mg). Respectively. Fraction 5 (16 g) was
subjected to an Rp-18 CC (MeOH-H2O, 30%−95%) to give 18 (88 mg) and 5 subfractions 5.1–5.5. Subfraction 5.4 (5 g)
was chromatographed on silica gel (petroleum ether-EtOAc,
20 : 1−1 : 2) to yield 11 (27 mg) and 12 (6 mg). 14 (11 mg),
22 (14 mg) and 27 (3 mg) were obtained by repeated silica gel CC, Sephadex LH-20 CC (MeOH) and further recrystallized from subfraction 5.3 (4 g). Fraction 6 (20 g) was subjected to an Rp-18 column (MeOH-H2O, 20%−95%)
to give 6 subfractions 6.1–6.6. Subfractions 6.3 (4 g) was chromatographed on silica gel (petroleum ether-Me2CO, 16 : 1−1 : 2) to yield 6 (8 mg), 8 (24 mg) and 23 (6 mg), respectively. Subfractions 6.4 (3 g) was chromatographed on silica gel (petroleum ether-EtOAc, 18 : 1−1 : 2) to give 7 (10 mg) and 9 (40 mg). 15 (8 mg) and 17 (17 mg) were obtained by repeated silica gel CC and further recrystallized from subfraction 6.5 (2 g).

5 Identification

**Compound 1** White amorphous powder (petroleum ether-EtOAc). ESI-MS m/z: 443 [M + H]+, C30H46O3. 1H NMR (CDCl3, 500 MHz): δ: 5.18 (1H, m, H-7), 4.96 (1H, m, H-24), 0.75, 0.87, 0.88, 0.91, 0.99, 1.35, 1.54 (each 3H × 1). 13C NMR (CDCl3, 100 MHz): δ: 121.9 (s, C-1), 21.3 (q, C-23), 21.1 (q, C-27), 29.7 (t, C-29), 27.0 (t, C-16), 26.9 (q, C-30), 25.7 (t, C-23), 25.3 (q, C-27), 24.1 (t, C-6), 21.4 (q, C-18), 21.3 (q, C-29), 17.4 (q, C-26), 17.3 (t, C-11), 12.4 (q, C-19). It was characterized as zizyberenalic acid by comparison of the physical and spectral data with the literature[3].

**Compound 2** White amorphous powder (petroleum ether-EtOAc). EI-MS m/z: 454, C30H46O3. 1H NMR (CDCl3, 500 MHz): δ: 5.18 (1H, m, H-7), 4.96 (1H, m, H-24), 0.75, 0.87, 0.88, 0.91, 0.99, 1.35, 1.54 (each 3H × 1). 13C NMR (CDCl3, 100 MHz): δ: 121.9 (s, C-1), 21.3 (q, C-23), 21.1 (q, C-27), 29.7 (t, C-29), 27.0 (t, C-16), 26.9 (q, C-30), 25.7 (t, C-23), 25.3 (q, C-27), 24.1 (t, C-6), 21.4 (q, C-18), 21.3 (q, C-29), 17.4 (q, C-26), 17.3 (t, C-11), 12.4 (q, C-19). It was characterized as 3-oxotrirucalla-7, 24-dien-21-oic acid by comparison of the physical and spectral data with the literature[3].

**Compound 3** White amorphous powder (petroleum ether-EtOAc). EI-MS m/z: 452, C30H46O3. 1H NMR (CDCl3, 500 MHz): δ: 9.70 (1H, s, H-2), 6.57 (1H, s, H-3), 4.76 (1Hs, H-30), 4.63 (1H, s, H-30), 1.77 (3H, s, H-29), 1.01 (3H, s, H-25), 1.00 (3H, s, H-26), 0.99 (3H, s, H-27), 0.94 (3H, s, H-24). 13C NMR (CDCl3, 125 MHz): δ: 187.0 (s, C-20), 150.1 (s, C-29), 109.8 (t, C-29), 63.0 (d, C-5), 56.2 (s, C-7), 52.2 (d, C-18), 49.4 (d, C-9), 46.9 (d, C-19), 42.5 (s, C-8), 38.2 (t, C-13), 37.1 (t, C-22), 35.2 (t, C-7), 32.3 (t, C-21), 23.6 (t, C-12), 21.0 (t, C-16), 19.3 (q, C-29), 18.9 (q, C-25), 17.6 (q, C-26), 14.7 (q, C-27). It was characterized as zizyberenalic acid by comparison of the physical and spectral data with the literature[3].

**Compound 4** White amorphous powder (petroleum ether-EtOAc). ESI-MS m/z: 471 [M + H]+, C30H46O4. 1H NMR (CDCl3, 500 MHz): δ: 9.72 (1H, s, H-2), 4.13 (1H, d, J = 8.5 Hz, H-3), 5.21 (1Hs, H-30), 4.98 (1H, s, H-30). 13C NMR (CDCl3, 100 MHz): δ: 191.4 (d, C-2), 182.3 (s, C-28), 163.3 (d, C-3), 157.3 (s, C-29), 150.1 (s, C-20), 109.8 (t, C-29), 63.0 (d, C-5), 56.2 (s, C-7), 52.2 (d, C-18), 49.4 (d, C-9), 46.9 (d, C-19), 42.5 (s, C-8), 38.2 (t, C-13), 37.1 (t, C-22), 35.2 (t, C-7), 32.3 (t, C-21), 23.6 (t, C-12), 21.0 (t, C-16), 19.3 (q, C-29), 18.9 (q, C-25), 17.6 (q, C-26), 14.7 (q, C-27). It was characterized as zizyberenalic acid by comparison of the physical and spectral data with the literature[3].

**Compounds**

1. Zizyberenalic acid
2. 3-oxotrirucalla-7, 24-dien-21-oic acid
3. Zizyberenal acid
4. 3-oxotrirucalla-7, 24-dien-21-oic acid

8a-epidioxy sterols from the marine sponge 

8a-ephedrine[19], 2', 6'-dihydroxy-4'-methoxyaceto-phenone[20], p-(aminomethyl)-benzoic acid[21], 4-hydroxy-3-methoxybenzoic acid[22] and 1-O-p-coumaroylglycerol[23], respectively, by comparison of the spectral data with those reported in the literatures. Compounds 24-25 were identified as β-sitosterol, poriferast-5-ene-3β, 4β-diol by comparing with the standard compounds. All the twenty-five compounds were isolated from 

Allophylus longipes for the first time.

References

【摘 要】目的:研究长柄异木患（Allophylus logipess）茎中的化学成分。方法:对长柄异木患茎甲醇提取物的乙酸乙酯部分进行色谱分离，根据光谱数据和理化性质确定各化合物的结构。结果:分离得到25个化合物，分别鉴定为：ycloart-24-ene-3β,26-diol (1)，3-oxotrirucalla-7,24-dien-21-oic acid (2)，zizyberenalic acid (3)，蛇藤酸 (4)，ent-4(15)-eudesmene-1β,6α-diol (5)，4(15)-eudesmene-1β,8a-diol (6)，4(15)-eudesmene-1β,5a-diol (7)，甲基埃斯特瑞 (8)，白桦脂醇 (9)，白桦脂酸 (10)，白桦脂醛 (11)，3β-hydroxy-5a,8a-epidioxyergosta-6,22-dien (12)，3-oxo-19α-hydroxyurs-12-en-28-oic acid (13)，熊果酸 (14)，东莨菪内酯 (15)，络皮啶 (16)，黄花菜木脂素 A (17)，香草醛 (18)，松柏醛 (19)，2’,6’-dihydroxy-4’-methoxyacetophenone (20)，p-(aminoalkyl)-benzoic acid (21)，香草酸 (22)，1-O-p-coumaroylglucose (23)，β-谷甾醇 (24)，poriferast-5-ene-3β,4β-diol (25)。结论:所有化合物均为首次从长柄异木患（Allophylus logipess）中分离得到。

【关键词】长柄异木患；化学成分

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