

Materials and Methods

M.p.s are uncorrected; IR (film, CHCl_3) and optical rotations were recorded on a Nicolet FT-170 SX and a JASCO-20C instrument, respectively. $^1\text{H-NMR}$ (400 MHz), $^{13}\text{C-NMR}$ (100.16 MHz), and DEPT spectra were recorded on a Bruker AM-400 NMR spectrometer in CDCl_3 with TMS as internal standard. EIMS and HRMS data were obtained on a HP 5988A-GC/MS and a VG ZAB-HS mass spectrometer, respectively.

Roots of *L. virgaurea* were collected in Zhang county, Gansu province, P. R. China in August 1988 and identified by Prof. Ru-Neng Zhao. A voucher specimen (no. 9882) has been deposited at the Herbarium of the Pharmacognosy Department, Lanzhou Medical College.

The pulverized, air dried roots of *L. virgaurea* (5.0 kg) were extracted twice (one week each time) with petroleum ether (60–90 °C)– Et_2O (2 : 1) at room temperature, and the extract was concentrated to afford a solid residue (250 g). 70 g of the solid extract were chromatographed on a silica gel (200–300 mesh, 950 g) column, eluted successively with a petroleum ether (60–90 °C)– EtOAc (50 : 1–1 : 1) gradient. Evaporation of solvent from the CC fractions (250 ml each) combined according to the TLC monitoring gave eight major fractions. Fraction II (2.1 g, eluted with petroleum ether– EtOAc , 45 : 1) was again chromatographed on silica gel (200–300 mesh, 60 g) eluted with petroleum ether– EtOAc (40 : 1) and finally purified by preparative TLC using petroleum ether– EtOAc (35 : 1) as development solvents (developed twice) to yield **4** (12 mg) and **6** (15 mg). Fraction III (1.6 g, eluted with petroleum ether– EtOAc , 40 : 1) was also purified on a silica gel (200–300 mesh, 45 g) column eluted with petroleum ether– EtOAc (35 : 1) and then followed by preparative TLC using petroleum ether (60–90 °C)– EtOAc (30 : 1) (developed three times) to yield **2** (6 mg). Compounds **3** (35 mg) and **5** (300 mg) were obtained from fraction V (7.8 g, eluted with petroleum ether– EtOAc , 15 : 1) by repeated column chromatography on silica gel (200–300 mesh, 160 g) eluted with petroleum ether– EtOAc (10 : 1). From fraction VII (1.6 g, eluted with petroleum ether– EtOAc , 6 : 1), compound **1** (5 mg) was obtained by repeated CC on silica gel (200–300 mesh, 50 g) eluted with petroleum ether– EtOAc (6 : 1) and then further purified by preparative TLC using petroleum ether– EtOAc (5 : 1) (developed two times).

Virgaurin B (**1**): yellowish needles, m.p.: 97–99 °C, $[\alpha]_{\text{D}}^{20}$: –42.00° (CHCl_3 , c 0.50); R_f = 0.30 (petroleum ether : ethyl acetate, 5 : 1); IR: $\nu_{\text{max}}^{\text{film}}$ = 3450 (OH), 2926, 2854, 1653 (C=C) and

1628, 1596, 1540, and 1456 (aromatic rings), 1375, 1347, 1230 and 1114 cm^{-1} ; EI-MS: m/z (%) = 458 (M^+ , 22), 403 (100), 229 (34), 228 (30; found 228.1161 in the HRMS), 175 (54), 91 (8), 77 (6), 55 (47); $^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): δ = 1.19 (3H, d, J = 7.0 Hz, H-15), 1.65 (3H, br. d, J = 5.4 Hz, H-15'), 1.74 (4H, m, H-2 and 3), 2.17 (3H, s, H-9'), 2.25 (3H, s, H-13), 2.35 (3H, s, H-10'), 2.60 (1H, m, H-1 β), 2.74 (2H, t, J = 7.8 Hz, H-11'), 3.00 (1H, m, H-1 α), 3.24 (1H, m, H-4), 4.41 (2H, dd, J = 17.0, 17.0 Hz, H-14a and 14b), 5.49 (2H, m, H-13' and 14'), 6.75 (1H, s, H-4'), 7.26 (1H, s, H-12). $^{13}\text{C-NMR}$ data and DEPT (Table 1).

Virgaurin C (**2**): yellowish gum, $[\alpha]_{\text{D}}^{20}$: +17.60° (CHCl_3 , c 0.50); R_f = 0.35 (petroleum ether : ethyl acetate, 30 : 1); IR: $\nu_{\text{max}}^{\text{film}}$ = 2925, 2853, 1650 (C=C), 1609, 1573, and 1452 (aromatic rings), 1338, 1226, and 1105 cm^{-1} ; EI-MS: m/z (%) = 486 (M^+ , 17), 431 (100; found 431.2234 in the HRMS; calcd. for $\text{C}_{28}\text{H}_{31}\text{O}_4$: 431.22), 432 (31), 361 (6), 346 (4), 243 (1), 188 (17), 173 (1), 55 (6); $^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): δ = 1.25 (3H, s, H-10), 1.64 (3H, br. d, J = 5.5 Hz, H-15), 1.94 (3H, s, H-9), 2.18–2.24 (2H, m, H-12), 2.77 (2H, t, J = 7.2 Hz, H-11), 4.16 (3H, s, OMe), 5.49 (2H, m, H-13 and 14), 7.20 (1H, s, H-8); $^{13}\text{C-NMR}$ data and DEPT (Table 1).

Calcolol (**3**): colorless platelet, m.p. 90–92 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): δ = 1.22 (3H, d, J = 7.3 Hz, H-15), 1.80–1.91 (4H, m, H-2 and 3), 2.41 (3H, s, H-13), 2.56 (3H, s, H-14), 2.63–2.72 (1H, m, H-1 β), 3.06 (1H, m, H-1 α), 3.28 (1H, m, H-4), 5.50 (1H, br. s, OH), 7.21 (1H, s, H-12); $^{13}\text{C-NMR}$ data and DEPT see references (2, 5). It should be mentioned that the chemical shifts of C-14 and C-15 methyl groups were erroneously interchanged in our previous report (2) comparison to the earliest report (5).

Acknowledgements

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References

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Erratum

O. Were, M. Benn, and R. Munavu, "Cinchona Alkaloid from *Dendrosenecio kilimanjari* subsp. *cottonii*", *Planta Medica* 63 (1997) 90–92.

The name M. Benn was included by the senior author among the authors of this letter without his authorisation. He wishes

it to be known that he dissociates himself from it, and is of the opinion that the conclusion that cinchonidine is a constituent of this *Dendrosenecio* is suspect (see O. S. Were, Ph. D. Thesis University of Calgary, 1991) and needs to be re-examined.