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CHEMICAL CONSTITUENTS FROM THE ROOTS OF *Senecio scandens*

C. F. Wang,[1] J. P. Li,[1,2] Y. B. Zhang,[1] and Z. Z. Zhang[1]*

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The chemical constituents of the roots of Senecio scandens *Buch.-Ham. grown in the Funiu mountains in China have been investigated. Four compounds were isolated and identified as* β*-sitosterol (**1**), pentacosanoic acid (**2**), 19*α*-H lupeone (**3**), and sucrose (**4**). The structures of these compounds were elucidated on the basis of chemical and spectroscopic evidence. 19*α*-H Lupeone (**3**) was isolated as a single compound and its structure established unambiguously by the spectral method for the first time, and ^{1}H and ^{13}C NMR data were assigned wholly by 1D and 2D NMR.*

Keywords: *Senecio scandens* Buch.-Ham., chemical constituents, 19α-H lupeone.

Senecio scandens Buch.-Ham. (Compositae) is one of the most important traditional medicinal plants and is distributed in many mountain areas in China. The plant has been used traditionally as a folk medicine for influenza, infections of the upper respiratory tract, infections of the urinary tract, and so on [1]. Some phytochemical studies on this plant regarding flavonoids, triterpenoids, lactones, and so on were reported previously [2–4]. During the first investigations on the roots of this plant grown in Funiu Mountains, Henan Province, China, four compounds were isolated and identified as β-sitosterol (**1**), pentacosanoic acid (**2**), 19α-H lupeone (**3**), and sucrose (**4**). The structures of these compounds were elucidated on the basis of chemical and spectroscopic evidence. The structure of compound **3** was reported in mixture form [5], prepared from 19α-H lupeol [6], but no detailed spectral data were reported. Compound **3** was isolated as a single compound by our group, and its structure was established unambiguously by the spectral method for the first time. Its ^{1}H and ^{13}C NMR data were assigned thoroughly by 1D and 2D NMR and comparison with the reference [7]. The stereochemistry of C-19 was determined by NOESY.

The roots of *Senecio scandens* (760 g) were ground and then extracted several times with 95% ethanol at room temperature and the solvent removed under reduced pressure. The extracts (60 g) were suspended in H_2O and re-extracted with petroleum ether and $CHCl_3$ successively, which gave a petroleum ether-soluble fraction (24 g), a $CHCl_3$-soluble fraction (12 g), and a water-soluble fraction (20 g). The $CHCl_3$ fraction was subjected to silica gel column chromatography (CC), and eluted with petroleum ether–ethyl acetate (from 50:1 to 1:1, v/v, gradually) to obtain five fractions (I–V). Compound **1** (β-sitosterol, 18 mg) [8] was crystallized from fraction II. Fraction III was subjected to silica gel CC with petroleum ether–ethyl acetate (10:1, v/v) repeatedly and gave compound **2** (pentacosanoic acid, 9 mg) [9]. Fraction I was subjected to silica gel CC, eluted with petroleum ether–ethyl acetate (30:1, v/v), to give a crystalline compound **3** (19α-H lupeone, 8 mg). The water-soluble fraction was subjected to Toyopearl HW-40 and Sephadex LH-20 CC, eluted with MeOH–H_2O (1:9–7:3, v/v, gradually) repeatedly, to give compound **4** (sucrose, 15 mg) [10].

1) School of Pharmaceutical Sciences of Zhengzhou University, Zhengzhou, Henan Province, 450051, P. R. China, fax: 86 371 67781908, e-mail: cfwang1040@126.com; zhenzhongz@126.com; 2) Department of Chemistry, Zhengzhou University, Henan Province, 450051, P. R. China. Published in Khimiya Prirodnykh Soedinenii, No. 2, pp. 224–225, March–April, 2011. Original article submitted December 24, 2009.

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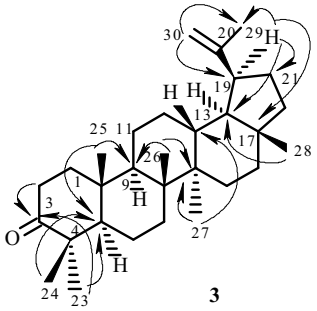
TABLE 1. The ^{13}C NMR and DEPT Data of **3** and Lupeone ($CDCl_3$, δ, ppm)

C atom	**3**	Lupeone [7]	C atom	**3**	Lupeone [7]	C atom	**3**	Lupeone [7]
1	39.6 (t)	39.6	11	21.6 (t)	21.5	21	27.3 (t)	29.9
2	34.2 (t)	34.1	12	23.9 (t)	25.2	22	41.9 (t)	40.0
3	218.2 (s)	217.9	13	49.5 (d)	38.2	23	26.5 (q)	26.6
4	47.5 (s)	47.2	14	41.2 (s)	42.9	24	21.1 (q)	21.0
5	54.9 (d)	55.0	15	32.7 (t)	27.4	25	15.8 (q)	15.8
6	19.7 (t)	19.6	16	21.6 (t)	35.6	26	16.6 (q)	15.4
7	33.6 (t)	33.6	17	44.5 (s)	43.0	27	16.4 (q)	14.4
8	42.1 (s)	40.8	18	54.9 (d)	48.3	28	16.1 (q)	18.0
9	49.5 (d)	49.8	19	46.4 (d)	47.9	29	25.1 (q)	19.3
10	37.2 (s)	36.9	20	149.8 (s)	150.7	30	110.0 (t)	109.2



3

Fig. 1. Key HMBC correlations of compound **3**.

Compound **3** was obtained as a white plate crystal (ethyl acetate). The molecular formula was established to be $C_{30}H_{48}O$ based on positive-ion APCI-MS (*m/z* 425.2 $[M + H]^+$) along with ^1H NMR and ^{13}C NMR data. The ^1H NMR spectrum displayed signals of seven methyl singlets (δ 0.72, 0.90, 0.92, 1.00, 1.03, 1.08, 1.72) and two olefinic protons (δ 4.78, s). ^{13}C NMR + DEPT (Table 1) showed signals of seven methyl carbons (δ 15.8, 16.1, 16.4, 16.6, 21.1, 25.1, 26.5), ten high-field methylene carbons (δ 19.7, 21.6, 21.6, 23.9, 27.3, 32.7, 33.6, 34.2, 39.6, 41.9), one low-field methylene carbon (δ 110.0), five high-field methine carbons (δ 46.4, 49.5, 49.5, 54.9, 54.9), five high-field quaternary carbons (δ 37.2, 41.2, 42.1, 44.5, 47.5), one olefinic quaternary carbon (δ 149.8), and one carbonyl carbon (δ 218.2). The above data of **3** were very similar to those of lupeone [7] except for the differences that the chemical shifts of two olefinic protons in the ^1H NMR spectrum of **3** were at δ 4.78 (2H, s) but those of lupeone were at δ 4.55, 4.69 (1H, d, J = 2.3 Hz), and the chemical shifts of C-13 (δ 49.5), C-15 (δ 32.7), C-16 (δ 21.6), C-18 (δ 54.9), and C-29 (δ 25.1) in the ^{13}C NMR spectrum of **3** shifted notably downfield or up-field compared to those of lupeone (C-13 (δ 38.2), C-15 (δ 27.4), C-16 (δ 35.6), C-18 (δ 48.3), and C-29 (δ 19.3)). These differences showed that the stereochemistry of C-19 of compound **3** may be different from that of lupeone, and the stereochemistry of C-19 of **3** could be 19α-H. This presumption was confirmed by the fact that the correlation peaks of H-30 (δ 4.78, 2H, s) and Me-29 (δ 1.72, 3H, s) with Me-28 (δ 0.72, 3H, s) were observed clearly, and that of H-19 (δ 2.68, 1H, m) with Me-28 was not seen in the NOESY spectrum of **3**. So, the structure of **3** was determined unambiguously as 19α-H lupeone. The ^1H NMR and ^{13}C NMR data were assigned thoroughly by the HSQC and HMBC spectra. The key HMBC correlations of **3** are shown in Fig. 1.

EXPERIMENTAL

General Methods. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a Bruker DRX-400 spectrometer. Chemical shifts were referenced to δ using tetramethylsilane (TMS) as an internal standard. The APCI mass spectrum was obtained using a Thermo Finningan LCQ DECA XP Plus spectrometer. Column chromatography (CC) was performed on silica gel (200–300 mesh or 300–400 mesh, Qingdao Marine Chemical Factory, Qingdao, China), Sephadex LH-20 (Pharmacia, Sweden), and Toyopearl HW-40 (TOSOH).

Plant Material. The roots of *Senecio scandens* were collected at Funiu Mountains, Henan Province, China, in August 2007 and identified by the authors. A voucher specimen (No. 20070801) has been deposited at the Department of Pharmaceutical Sciences, Zhengzhou University.

Characteristics of 19α-H Lupeone (3). White plate crystal. Positive APCI-MS *m/z*: 425.2 $[M + H]^+$. ^1H NMR ($CDCl_3$, δ, ppm): 0.72 (3H, s, Me-28), 0.90 (3H, s, Me-25), 0.92 (3H, s, Me-26), 1.00 (3H, s, Me-27), 1.03 (3H, s, Me-24), 1.05 (1H, m, H-22b), 1.08 (3H, s, Me-23), 1.25 (1H, m, H-7b), 1.29 (1H, m, H-15b), 1.29 (1H, m, H-5α), 1.31 (1H, m, H-9α), 1.38 (1H, m, H-13β), 1.39 (1H, m, H-18α), 1.42 (1H, m, H-1b), 1.42 (1H, m, H-7a), 1.47 (2H, m, H_2-6), 1.47 (2H, m, overlapped, H_2-12), 1.48 (1H, m, H-16b), 1.49 (1H, m, H-15a), 1.51 (1H, m, H-11b), 1.51 (1H, m, H-16a), 1.62 (1H, m, H-22a), 1.65 (1H, m, H-11a), 1.72 (3H, s, Me-29), 1.83 (2H, m, H_2-21), 1.92 (1H, m, H-1a), 2.38 (1H, m, H-2b), 2.48 (1H, m, H-2a), 2.68 (1H, m, H-19α), 4.78 (2H, s, H_2-30). ^{13}C NMR data appear in Table 1 and key HMBC correlations are in Fig. 1.

REFERENCES

1. The Group of Chinese Herbal Medicine Assembly of Whole Country. Chinese Herbal Medicine Assembly of Whole Country (Scroll), People′s Medical Press, Beijing, 1977, p. 213.
2. J. Shi, F. Zhang, H. Y. Ma, C. H. Wang, G. X. Yu, M. Zhang, C. F. Zhang, and Z. T. Wang, *Chin. J. Chin. Mater. Med*., **32**, 1600 (2007).
3. L. X. Chen, H. Y. Ma, M. Zhang, C. F. Zhang, and Z. T. Wang, *Chin. J. Chin. Mater. Med*., **31**, 1872 (2006).
4. J. Shi, L. Yang, C. H. Wang, and Z. T. Wang, *Biochem. Syst. Ecol*., **35**, 901 (2007).
5. A. Branco, A. C. Pinto, and F. R. Braz, *An. Acad. Brasil. Cienc.*, **76**, 505 (2004).
6. U. Viqar, S. B. Ahmad, and V. M. Faryal, *Planta Med*., **22**, 521 (1985).
7. W. Z. Liu, Q. G. Ma, X. F. Gu, and G. W. Qin, *Nat. Prod. Res. Dev.*, **15**, 396 (2003).
8. D. F. Yu, B. H. Hu, H. Sha, G. H. Zheng, and L. C. Zhou, *Chin. Trad. Herb. Drugs*, **22**, 3 (1999).
9. L. M. Chen, P. Xie, Q. Q. Xiao, Q. H. Liu, and X. Luo, *Chin. Trad. Herb. Drugs*, **38**, 815 (2007).
10. W. S. Feng, Y. Z. Wang, and X. K. Zheng, *Structural Elucidation of Chemical Constituents of Traditional Chinese Medicine*, Science Press, Beijing, 2008, p. 80.