Chinese Chemical Letters Vol. 14, No. 2, pp 176 – 178, 2003
http://www.imm.ac.cn/journal/ccl.html

A New Steroid from *Polygonum nodosum* Pers

Shang Zhen ZHENG[1]*, Tong SHEN[2], Xu Wei SHEN[1], Zhong Jian JIA[2]

[1]College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070
[2]National Laboratory of Applied Organic Chemistry, Institute of Organic Chemistry, Lanzhou University, Lanzhou 730000

Abstract: A new steroid named as Zhonghualiaoine I (**1**) was isolated from *Polygonum nodosum* Pers (Chinese name "Zhonghualiao", Berberidaceae). Its structure was deduced on the basis of its spectral data.

Keywords: Polygonum nodosum, isolation, elucidation.

Polygonum nodosum Pers which has a strong effect on stopping bleeding, making blood circling and which also is a traditional chinese folk drug for treating diarrhea, lung carcinoma, *etc*[1,2]. But few is known about its chemical constituents. We have carried out a detailed chemical investigation and have isolated one new steroid. In this paper, we report the isolation and structural determination of **1**. The samples of *Polygonum nodosum* Pers were collected in Gansu of China. The dried and powdered leaves, stems and roots of the *Polygonum nodosum* Prers were extracted three times with 75% EtOH at room temperature (each process lasting 7 days), the EtOH extract was extracted with EtOAc and CH_3Cl-MeOH (1:2, v/v) three times, respectivly, under reflux. CH_3Cl-MeOH extraction was column chromatographed on silica gel using a CH_3Cl-MeOH gradient eluted, them examined by TLC. Resulted in the separation of a new steroid compound, named as Zhonghualiaoine **I** (**1**).

Compound **1** was obtained as white needles. It was shown by HRMS to have the molecular formula $C_{29}H_{46}O_4$, based on the HRMS of the molecular ion peak at *m/z* 458.3602 (calcd: 458.3610), indicating seven degrees of unsaturation, ascribed to one carbonyl group, one epoxide ring, four steroide ring, and one threemembered ring. The usual colour test indicated **I** to be a steroid. ^{1}H-NMR and ^{13}C-NMR(**Table 1**) of **1** revealed signals due to six methyls, seven methenes, twelve methines and four quaternary carbons, which suggest the presence of 29 carbons. Its ^{1}H-NMR indicated the presence of six methyl groups at δ0.64 (s, 3H, 18-CH_3), 1.26 (s, 3H, 19-CH_3), 0.94 (d, 3H, *J*=6.8, 26-CH_3), 0.928 (d, 3H, *J*=6.8, 27-CH_3), 1.01 (d, 3H, *J*=7.5, 21-CH_3), 0.99 (d, 3H, *J*=6.0, 29-CH_3). A series of proton signals at δ 0.66-3.62 were attributed to resonances of overlapping of more methene and methine of framework of steroid. The IR bands at 1745 cm^{-1} indicated the presence of one fivemembered ring ketone with

*E-mail:ZhengSZ@nwnu.edu.cn

carbonyl group. In the IR spectrum, signals typical of hydroxy (3396, 1060 cm^{-1}) and ether band (C-O-C, 1106 cm^{-1}) were observed.

The central framework of **1** was substantiated by COSY, HMBC correlations and by comparing the ^{1}H and ^{13}CNMR date with those of **1** (**Table 1**). Besides other signals showed resonances, due to one epoxide ring and one carbonyl group. One more oxygen atom had to be placed between C_5 and C_6 to form a epoxide. The ketone functionality at C_{16} was confirmed by its HMBC correlations to H_2-15 and H-17. Another one-proton signal appeared as a broad of multilets at δ 1.20 was diagnostic of the C-8 methine proton, while another downfield signal at δ 3.26 (d, *J*=4.5Hz) was assigned to the C-6 methine proton. Two hydrogen at δ 3.60 (d, *J*=4.5Hz) and 3.62 (d, *J*=4.5Hz) was assigned to the C-1, C-3 methine, its downfield chemical shift values suggested the presence of a geminal hydroxyl functionality at C-1 and C-3[3,4].

The EIMS of **1** gave a significant fragment ion peak at *m/z*=319 (16). Based on the EIMS, the molecular formula of side-chain was established to be $C_{10}H_{19}$, indicating one degree of unsaturation. In the IR spectrum, signal of double band was not observed, implying the presence of one ring. ^{1}HNMR revealed three highfield protons at δ -0.265 (ddd, 1H, *J*=4.5, 8.0, 4.5Hz) and δ 0.66 (m, 2H), corresponding to a threemembered ring structure. In addition, coupling of ddd is at 4.5Hz~8.0Hz, reducing the position of the threemembered between C-23 and C-24[3,4]. The fragments of **1** at *m/z* 361, 374 and 402 in the MS further specified that the threemembered was linked to C-23 and C-24, (**Figure 1**).

The stereochemistry of compound **1** was determined on the basis of the NOESY (**Figure 1**) information as follows: compound **1** showed an $[\alpha]_D^{20}$ +20.8 (*c* 0.2,MeOH), the positive sign of optical rotation suggested that the C-3 methine proton has an α-orientation, while the C-8 methine protone, C-18 and C-19 methyl groups are β-oriented[4]. The C-1 methine proton (δ3.62) showed a cross-peak with the C-3 methine proton (δ 3.64) which suggested the α-stereochemistry for the C-1 methine proton and thus the β-stereochemistry for the C-1 hydroxyl. NOE cross-peak beteen H-8 (δ 1.20), H-18 (δ 0.64) and H-19 (δ 1.26). The C-6 methine proton (δ 3.26), exhibited with the C-8 methine proton (δ 1.20) and C-19 methyl proton (δ 1.26), indicating that the C-5 / C-6 epoxy functionality has the α-orientation. In the NOESY spectrum (**Figure 1**) of **1**.The correlations between H-3 and H-1, 4 suggested that ring A has a chair conformation, H_3-21 did not give correlation with H_3-18, and H_3-21 was found to exhibit correlation with H-14, 17. Thus, H-14, 17 should be placed on the α-phase. Detailed consideration of molecular models, structure **1** was established for this new natural product named as Zhonghualiaoine **1** (**Figure 1**).

Figure 1 Structure of compound **1**

Zhonghualiaoine **1** Key NOESY of compound **1**

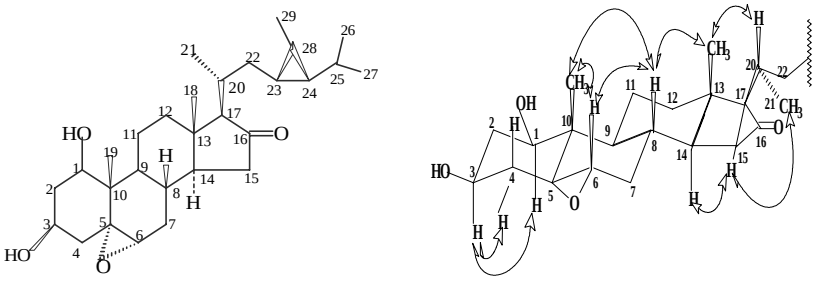

Table 1 ^{1}H-NMR and ^{13}C-NMR data of compound 1(δ ppm, $CDCl_3$)

Carbon	H-1	δ_H	δ_C	Carbon		δ_H	δ_C
1		3.60(br,s)	74.10	16			206.75
2	H-2	1.51(m), 2.11(m)	35.40	17	H-17	1.60(m)	65.09
3	H-3	3.62(t)	71.68	18	H-18	0.64(e)	11.7
4	H-4	1.45(d), 1.94(d)	40.80	19	H-19	1.26(s)	19.50
5			61.20	20	H-20	1.29(m)	37.91
6	H-6	3.26(d)	60.10	21	H-21	1.01(d)	14.36
7	H-7	1.78(m), 2.41(m)	31.39	22	H-22	0.66(m)	35.44
8	H-8	2.82(dt)	38.27	23	H-23	0.46(m)	19.42
9	H-9	1.28(m)	45.72	24	H-24	-0.128(ddd)	35.00
10			49.56	25	H-25	1.43(m)	33.18
11	H-11	1.43(m), 1.78(m)	20.56	26	H-26	0.94(d)	22.01
12	H-12	1.40(m), 1.65(m)	36.19	27	H-27	0.928(d)	22.10
13			41.17	28	H-28	0.46(m)	15.30
14	H-14	2.36(m)	48.08	29	H-29	0.99(d)	18.55
15	H-15	1.78(dd),2.14(dd)	38.27				

Acknowledgments

The work was supported by the Northwest Normal University-Bring Forth new Idea Project of Science and Technology, P. R. China

References

1. *Jiangsu New Medical College Dictionary of traditional Chinese Druges*, (Changhai Science and Technology Press), **1977**, p2203.
2. K. E.Yaacob,J.Essent, *Oil Res*., **1990**, *1*, 167.
3. D. R,Abimael,R.Jocelyn,B.Anna, *Tatrahedron Lett.*, **1998**, *39*, 7645.
4. N. Samina, G. K. Russell, N. Ramaswamy, *Tatrahedron Lett*., **2000**, *41*, 6035.

Received 16 May, 2002