Chinese Chemical Letters Vol. 14, No. 12, pp 1259 – 1260, 2003 1259
http://www.imm.ac.cn/journal/ccl.html

A New Furostanol Glycoside from *Polygonatum odoratum*

Hai Lin QIN*, Zhi Hong LI, Peng WANG

Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050

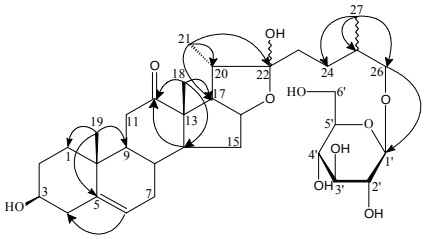
Abstract: A new furostanol component glycosylated only at C-26 was isolated from the rhizomes of *Polygonatum odoratum* (Mill.) Druce, and its structure was characterized as 22-hydroxy-25(*R* and *S*) furost-5-en-12-on-3β, 22, 26-triol 26-*O*-β-*D*-glucopyranoside on the basis of spectroscopic techniques and chemical methods.

Keywords: *Polygonatum odoratum* (Mill.) Druce, furostanol monoglycoside.

The crude glycoside fraction obtained from the ethanolic extract of the rhizomes of *Polygonatum odoratum* (Mill.) Druce was chromatographed on silica gel to afford a new steroidal ingredient **1**.

Compound **1**, colorless needles, mp 142-143℃, $[\alpha]_D^{17}$ -0.024 (*c* 0.11, MeOH). The IR spectrum showed a strong broadened absorption band at 3425 cm^{-1} for hydroxy groups and a sharpened absorption band at 1707 cm^{-1} for carbonyl group. Its molecular formula was indicated to be $C_{33}H_{52}O_{10}$ by the data at *m/z* 647$[M+K]^+$, 631$[M+Na]^+$, 591$[M-H_2O+H]^+$ from positive FAB-MS and at 631.3487$[M+Na]^+$ (calcd. for $C_{33}H_{52}O_{10}Na$ 631.3458), 591.3536$[M-H_2O+H]^+$ (calcd. for $C_{33}H_{51}O_9$ 591.3534) from high resolution FAB-MS, and it was assumed to be a furostanol saponin on the basis of above data[1]. The signals at δ_H 4.17(d, 1H, J=8.0 Hz) and δ_C 104.6 (d) in the ^1H, ^{13}C and DEPT NMR spectra of compound **1** indicated that **1** possessed a monoglycosidic structure with a β- sugar unit. The signals in the ^{13}C NMR spectrum due to its aglycone moiety (see **Table 1**) indicated that it is 22-hydroxy-furost-5-en-12-on-3β, 22, 26-triol[2],

Figure 1 The structure and key HMBC correlation of **1**



* E-mail:qinhailin@imm.ac.cn

Table 1 ^{13}C NMR data for **1** (125MHz, in CD_3OD)

C	δ	DEPT	C	δ	DEPT	C	δ	DEPT
1	38.1[a]	CH_2	12	215.8	C	23	32.06, 32.12	CH_2
2	32.1[b]	CH_2	13	56.4	C	24	28.87, 28.93	CH_2
3	72.1	CH	14	57.3	CH	25	35.0, 35.1	CH
4	42.8	CH_2	15	32.6[b]	CH_2	26	75.8, 76.0	CH_2
5	142.2	C	16	80.9	CH	27	17.2, 17.4	CH_3
6	122.1	CH	17	56.0, 56.1	CH	1′	104.6	CH
7	31.3[b]	CH_2	18	16.4	CH_3	2′	75.2	CH
8	32.1	CH	19	19.3	CH_3	3′	78.1	CH
9	53.9	CH	20	41.6, 41.8	CH	4′	71.7	CH
10	38.4	C	21	14.7, 14.8	CH_3	5′	78.0	CH
11	38.3[a]	CH_2	22	114.0	C	6′	62.8	CH_2

[a,b]Signals may be interchanged respectively.

while the signals due to its sugar moiety were identical with those of C-26 linked glucose[2]. The TLC of the acidic hydrolysate of **1** confirmed the liberating of glucose from this compound. The glycosylation of **1** was located at C-26 on the basis of the carbon signals at δ 76.0 (C-26) in the ^{13}C NMR spectrum, and this was confirmed by the HMBC experiments (see **Figure 1**). In addition, the ^1H NMR spectrum of **1** also showed the characteristic signals at δ 1.01(d, 3H, J=6.5Hz, CH_3-21), 1.08(s, 3H, CH_3-18), 1.09 (s, 3H, CH_3-19), 2.58 (m, 1H, H-14), 3.71 (m, 1H, H-26a), 4.26 (ddd, 1H, J=5.5, 7.0, 8.5Hz, H-16) and 5.35 (m, 1H, H-6). Besides, two low-intensity doublet signals ascribed to CH_3-27 at δ 0.89 and 0.90 (total 3H, both J=6.6Hz) were detected, and this fact, along with the pairs of the signals for C-17,20,21,23,24,25,26 and 27 in the ^{13}C NMR spectrum, clearly revealed that the 25 (*R*) and 25 (*S*) epimers of **1** were existed. The signal at higher field was corresponding to the 25 (*R*) configuration and the lower one to the 25 (*S*)[3]. Moreover, the 25 (*R*) epimer was somewhat more than the 25 (*S*) from their ^1H NMR signal intensities. All of the signals in the ^1H and ^{13}C NMR spectra were unambiguously assigned by ^1H-^1H COSY, HMQC and HMBC experiments. Consequently, the structure of **1** was assigned as 22-hydroxy-25 (*R* and *S*)-furost-5-en-12 -on-3β, 22, 26-triol 26-*O*-β-*D*-glucopyranoside.

To the best of our knowledge, and according to the literature[4], all of the furostanol glycosides obtained by now were simultaneously glycosylated with two sugar chains, one of them must be at C-26, the other at C-3. So this is the first report of the furostanol monoglycoside glycosylated only at C-26.

Acknowledgment

Project 02-03zp09 was supported by the Science Foundation of State Administration of Traditional Chinese Medicine, P.R. China

References

1. F. Liang, L. J. Li, Z. Abliz, *et al*., *Rapid. Commun. Mass Spectrom*, **2002**, *16*, 1168.
2. X. C. Li, C. R. Yang, M. Ichikawa, *et al*., *Phytochemistry*, **1992**, *31*(10), 3559.
3. M. Yoshikawa, T. Murakami, H. Komatsu, *et al*., *Chem. Pharm. Bull*.,**1997**, *45*(1), 81.
4. X. S. Yao, *Chemistry on Natural Medicines*, People's Health Press, Beijing, **2000**, p 407.

Received 23 January, 2003