Chinese Chemical Letters Vol. 14, No. 9, pp 920 – 922, 2003
http://www.imm.ac.cn/journal/ccl.html

A New Flavonol Diglycoside from *Pyrrosia petiolosa*

Yong Chun YANG, Chun YANG, Shun Yan MO, Jian Gong SHI*

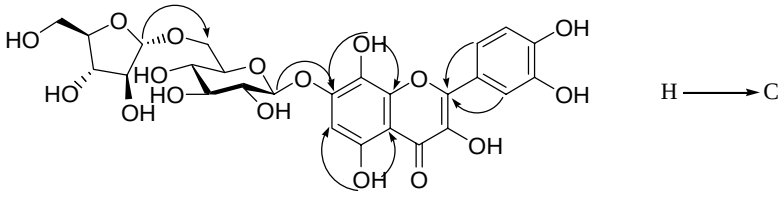
Institute of Materia Medica, Chinese Academy of Medical Sciences and
Peking Union Medical College, Beijing 100050

Abstract: A new flavone diglycoside, named as pyrropetioside A **1** was isolated from *Pyrrosia petiolosa*. Its structrue was elucidated as 7-O-[6-O-(α-L-arabifuranosyl)-β-D-glucopyranosyl]-gossypetin by means of chemical and spectroscopic methods including IR, MS, 1D and 2D NMR techniques.

Keywords: *Pyrrosia petiolosa*, flavone diglycoside, pyrropetioside A.

In the Chinese Pharmacopoeia[1], three *Pyrrosia* species *P. lingua*, *P. sheareri* and *P. petiolosa*, are used as sources of the Chinese traditional remedy "Shiwei" which is used for the treatments of swell, urocystitis, urinary calculus, bloody urine, cough and bronchitis, *etc*[1,2]**.** *P. petiolosa* was found to be the commonest used one in our recent investigation in Chinese markets of 16 cities. In order to determine the indicative components of "Shiwei" and to control its quality by HPLC fingerprint techniques, we carried out a systematic study of chemical constituents of *P. petiolosa* since only several usural plant metabolites were reported from this plant[3]. From the ethanolic extract, a new flavone diglycoside named as pyrropetioside A **1** was isolated. We describe here the isolation and structural elucidation of this compound.

Figure 1 The key HMBC correlations of **1**



The air-dried and grounded leaves of *P. petiolosa* were extracted with 95% ethanol, the concentrated extract was suspended in water, and then partitioned with EtOAc. The water layer was subjected to chromatography on macro porous resin, normal

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

phase silica gel, and Sephadex LH-20 successively to yield compound **1** as a yellow powder, m.p. 188-190 °C, $[\alpha]_D^{22}$ -56 (*c* 0.20, MeOH). Its IR spectrum（KBr）showed absorption bands for hydroxyl (3388cm^{-1}), conjugated carbonyl (1658cm^{-1}) groups and aromatic rings (1614 and 1514 cm^{-1}). The FABMS spectrum exhibited a molecular ion peak at *m/z* 613 $[M+H]^+$, and the molecular formula was determined as $C_{26}H_{28}O_{17}$ by HRFABMS at *m/z* 613.1418 (calcd. for $C_{26}H_{29}O_{17}$ 613.1405). The ^{1}H NMR spectrum of **1** in DMSO showed signals attributed to a 1, 3, 4-trisubstituted phenyl moiety at δ 7.74 (d, 1H, J=1.8 Hz, 2′-H), 7.61 (dd, 1H, J=8.7 and 1.8 Hz, 6′-H), 6.88 (d, 1H, J=8.7 Hz, 5′-H), an isolated aromatic proton at δ 6.62 (s, 1H, 6-H), and five exchangeable phenolic hydroxyl protons at δ 11.88 (s, 1H, 5-OH), 9.60 (s, 1H, 3′-OH), 9.42 (s, 1H, 3-OH), 9.32 (s, 1H, 4′-OH) and 8.57 (s, 1H, 8-OH), as well as signals assignable to two anomeric proton at δ 4.81 (d, 1H, J=7.2 Hz, 1″-H) and 4.72 (s, 1H, 1‴-H) together with 11 glycosyl protons between δ 3.9-3.1. The ^{13}C NMR and DEPT spectra of **1** displayed 28 carbon signals which consisted of characteristic 15 sp^2 carbons of a flavone aglycone and 13 sp^3 carbons of two glycosyl moieties (see **Table 1**). The above spectral data revealed that **1** is a flavone di-glycoside with an α and a β sugar units. The ^{1}H and ^{13}C NMR spectral data were unambiguously assigned by HMQC and HMBC experiments. The signals assigned to the aglycone moiety were in good agreement with those of gossypetin[4], while the signals assigned to sugar units revealed the presences of a terminal α-L-arabifuranosyl unit[5] and a 6-substituted β-D-glucopyranosyl unit[6]. After acidic hydrolysis of **1,** the Co-TLC and Co-PC confirmed the releasing of arabinose and glucose from **1**. In the HMBC spectrum (see **Figure 1**) long range correlations from H-1″ to C-7 and H-1‴ to C-6″ unequivocally established that a disaccharide α-L-arabifuranosyl(1→6)-β-D-glucopyranosyl moiety was located at C-7 of the aglycone. Accordingly, the structure of **1** was determined as 7-O-[6-O-(α-L-arabifuranosyl)-β-D-glucopyranosyl]-gossypetin.

Table 1 ^{1}H and ^{13}C NMR data of compound **1** [a]

Aglycone moiety			Sugar moiety		
No.	δ_H	δ_C	No.	δ_H	δ_C
2		147.2	1″	4.81 d (7.2)	101.2
3		135.6	2″	3.38 m	73.2
4		176.1	3″	3.60 m	75.6
5		151.3	4″	3.15 dd (7.8, 7.5)	69.9
6	6.62 s	97.8	5″	3.57 m	75.4
7		150.1	6″	3.91 br d (10.2) 3.40 dd (10.2, 7.8)	67.0
8		126.6			
9		143.8	1‴	4.72 s	108.5
10		104.6	2‴	3.77 m	81.9
1′		122.0	3‴	3.62 m	77.1
2′	7.74 d (1.8)	115.4	4‴	3.72 m	83.8
3′		144.9	5‴	3.53 m 3.36 m	61.2
4′		147.7			
5′	6.88 d (8.7)	115.1			
6′	7.61 dd (8.7, 1.8)	120.1			

[a] NMR data were measured in DMSO at 500 MHz for proton and at 125 MHz for carbon. Proton coupling constants (*J*) in Hz are given in parenthesis. The assignments were based on DEPT, ^{1}H-^{1}H

COSY, HMQC and HMBC experiments.

Acknowledgments

The authors are grateful to professor Ablez zeper Institute of Materia Medica, Chinese Academy of Medical Sciences, for mass spectra measurements, and financial support from the Ministry of Sciences and Technology of China (Grant No.99-929-01-26).

References

1. National Pharmacopoeia Committee, *Pharmacopoeia of People's Republic of China*, Chemical Industry Press, Beijing, **2000**, *1*, p. 68.
2. Jiangsu New Medical College, *Dictionary Of Traditional Chinese Medicine*, Shanghai Science and Technology Publishing House, Shanghai, **1977**, p. 579-581.
3. J. Li，*Chinese Traditional And Herbal Drugs*，**1992**, *23* (7), 348.
4. T. Schoelly, I. Kapetanidis, *Sci. Pharm.*, **1993**, *61* (4), 277.
5. P. A. J. Gorin, M. Mazurek, *Can. J. Chem*., **1975**, *53* (8), 1212.
6. K. R. Markham, B. Ternal, R. Stanley, H. Geiger, T. J. Mabry, *Tetrahedron*, **1978**, *34* (9), 1389.

Received 29 August, 2002