Chinese Chemical Letters Vol. 16, No. 6, pp 771-773, 2005
http://www.imm.ac.cn/journal/ccl.html

A New Bisxanthone from *Hypericum japonicum* Thunb. ex Murray

Peng FU, Wei Dong ZHANG*, Ting Zhao LI, Run Hui LIU, Hui Liang LI, Wei ZHANG, Hai Sheng CHEN

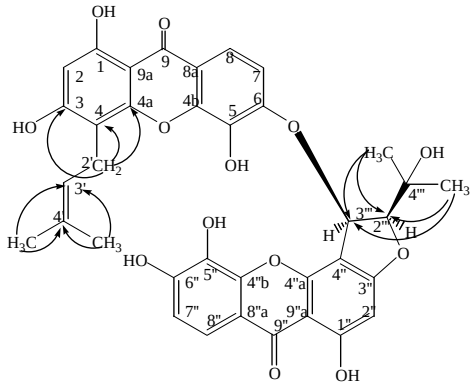
Department of Natural Medicinal Chemistry, School of Pharmacy, Second Military Medical University, Shanghai 200433

Abstract: A new bisxanthone, named bijaponicaxanthone C, was isolated from the whole plant of *Hypericum japonicum*. The structure was elucidated as 6-[1",5",6"-trihydroxy-2"'-(*β*-hydroxy-*β*-methylethyl)-2"',3"'-dihydrofuran(5"',4"',3",4")xanthone-3"'-oxyl]-1,3,5-trihydroxy-4-isoprenylxanthone (**1**) on the basis of the spectral and chemical evidences.

KeyWords: *Hypericum japonicum*, bisxanthone, 6-[1",5",6"-trihydroxy-2"'-(*β*-hydroxy-*β*-methylethyl)-2"',3"'-dihydrofuran(5"',4"',3",4")xanthone-3"'-oxyl]-1,3,5-trihydroxy-4-isoprenylxanthone, bijaponicaxanthone C.

Hypericum japonicum Thunb. ex Murray is a Chinese medicinal plant widely distributed in central and east China. The whole plant is being used for the treatment of several bacterical diseases, infectious hepatitis, gastrointestinal disorder and tumors[1]. It was reported that many kinds of compound, such as xanthones, chromenes, flavanonols, dipeptide derivatives and phloroglucinol derivatives[2-5], have been isolated previously. In this paper, we report the characterization of a new bisxanthone obtained from the whole plant of *Hypericum japonicum* and its structure was determined by UV, IR, HREIMS, 1D and 2D-NMR spectra.

Figure 1 The structure and the key correlations in HMBC of compound **1**



* E-mail: WDZhangY@hotmail.com

The ethanol extract of the whole plant of *Hypericum japonicum* (23 kg) was evaporated *in vacuo*. The residue was suspended in water, and then partitioned with petroleum ether, $CHCl_3$ and EtOAc, successively. The EtOAc extract (280 g) was further seperated by repeated colum chromatography on silica gel, eluted with $CHCl_3$:CH_3OH (10:1) to afford compound **1** (**Figure 1**).

Compound **1**, was obtained as a yellow powder, mp 240-245°C (decomposition). The ion at *m/z* 670.08 [M^+] of ESIMS is in agreement with the formula $C_{36}H_{30}O_{13}$, which was confirmed by HRESIMS, showing the $[M+H]^+$ ion at *m/z* 671.1768, calculated for $C_{36}H_{31}O_{13}$: 671.1765. The UV spectrum showed the characteristic absorption of chromenoxanthones (253 and 324 nm). In the IR the adsorption of phenolic hydroxy

Table 1 NMR data and major correlation of HMBC and HMQC of **1** (in DMSO-d_6)

Position	^{13}C-NMR	^{1}H-NMR (δppm, *J*Hz)	HMBC (H/C)
1	160.4		1-OH
2	97.7	6.24 (IH, s)	1-OH
3	162.9		2'-H
4	106.4		2-H; 2'-H
4a	154.1		2'-H
4b	145.7		8-H
5	131.6		7-H
6	149.4		8-H
7	113.3	7.03 (1H, d, *J*=9 Hz)	
8	116.7	7.62 (1H, d, *J*=9 Hz)	
8a	113.6		7-H
9	179.6		8-H
9a	101.5		1-OH
2'	21.1	3.37 (2H, d, *J*=7 Hz)	
3'	122.4	5.42 (IH, t, *J*=7 Hz)	2'-H; 4'-Me
4'	131.0		2'-H; 4'-Me
4'-Me	17.7; 17.9	1.64,1.77 (each 3H, s)	3'-H; 4'-Me
1"	157.2		
2"	97.7	6.30 (1H, s)	
3"	162.7		
4"	101.7		2"-H
4"a	150.2		
4"b	145.9		8"-H
5"	132.7		7"-H
6"	151.9		8"-H
7"	113.0	6.94 (1H, d, *J*=9 Hz)	
8"	115.7	7.51 (1H, d, *J*=9 Hz)	
8"a	112.8		7"-H
9"	179.9		2"-H; 8"-H
9"a	103.1		
2"'	79.2	5.92 (1H, br)	4""-Me
3"'	71.0	5.02 (1H, br)	4""-Me
4"'	70.2		
4"'-Me	28.4; 25.5	1.31, 1.26 (each 3H, s)	4""-Me
1-OH		12.95	
1"-OH		13.40	
4"'-OH		4.35	

The assignment was based on DEPT, ^{1}H-^{1}H COSY, HMBC and HMQC experiments. 500MHz for ^{1}H-NMR, 125MHz for ^{13}C-NMR, HMBC, HMQC.

groups (3422 cm^{-1}) and a conjugated carbonyl group (1648 cm^{-1}) were observed. The EIMS spectrum showed two groups of fragment at *m/z* 311, 326 and 283. These data indicated that it possessed two similar prenylated xanthones, combining its ^{1}H NMR and ^{13}C NMR. One xanthone fragment resembled to the known compound 1, 3, 5, 6-tetrahydroxy-4-prenylxanthone[3]. The downfield protons at δ5.42 (t, 1H, *J* = 7 Hz, H-3'), 3.37 (d, 2H, *J* = 7 Hz, H-2') and the six proton singlets at δ1.64, 1.77 (4'-Me) suggested the presence of a isoprenyl. The AB-system aromatic proton signal at δ7.03 (d, 1H, *J* = 9 Hz) and δ 7.62 (d, 1H, *J* = 9 Hz) were due to H-7 and H-8, respectively, whereas the aromatic singlet at δ 6.24 (1H) were due to H-2[3]. The other group of aromatic proton signal at δ 6.94 (d, 1H, *J* =9 Hz, H-7''), δ 7.51 (d, 1H, *J* = 9 Hz, H-8'') and δ 6.30 (s, 1H, H-2'') were similar to those of the xanthone fragment mentioned above[3]. Combining its DEPT and 2D NMR, the proton signals at δ5.92 (brs, 1H, H-2'''), 5.02 (brs, 1H, H-3'''), 4.35 (brs, 1H, 4'''-OH), and 1.26, 1.31 (s, each 3H, 4'''-Me) indicated the presence of a 2,3-dihydro-2-(1-hydroxy-1-methylethyl)-3-oxyl-furan ring[3]. The stereochemistry of **1** was established by NOESY spectrum. Clear NOE correlations between H-8'' and 4'-Me, H-2''' and H-3''' indicated H-2''' and H-3''' were in α-configuration. In comparison with those of 1, 3, 5, 6-tetrahydroxy-4-prenylxanthone, the downfield shift (+0.12 ppm) for H-7 and the upfield shift (−5.3 ppm) for C-6 indicated a C_6-O-$C_{3'''}$ linkage[3]. Thus, compound **1** was established as 6-[1'',5'',6''-trihydroxy-2'''-(β-hydroxy-β-methylethyl)-2''',3'''-dihydrofuran (5''', 4''', 3'',4'')xanthone-3'''-oxyl]-1,3,5-trihydroxy-4-isoprenylbisxanthone, named bijaponicaxanthone C. From its HMQC and HMBC, all of the carbon signals were assigned (**Table 1**).

Acknowledgments

The research work was supported by the National 863 program of China (2003AA2Z3507) ; Science and Technology Developping Foundation of Shanghai (02DZ19147, 01DJ19010). Authors thank Professor Han Chen ZHENG (Department of Pharmacognosy, School of Pharmacy, Second Military Medical University) for collecting *Hypericum japonicum*.

References

1. *Lexicon of Traditional Chinese Medicine* , Shanghai Sci-Tech. Press. **1977**, *1*, 813.
2. Editorial Board of Zhong Hua Ben Cao of State Administration of Traditional Chinese Medicine. *Zhong Hua Ben Cao* , Shanghai Sci-Tech. Press., 1999, *3*,598
3. Q. L. Wu, S. P. Wang, L. J. Du, *et al.*, *Phytochemistry*, **1998**, *49*(5),1395.
4. K. Ishiguro, S. Nagata, H. Oku, *et al.*, *Planta Med*, **2002**, *68*,258
5. L. H. Hu, C. W. Khoo, J. J. Vittal, *et al.*, *Phytochemistry*, **2000**, *53*(6),705

Received 8 June, 2004