Chinese Chemical Letters Vol. 12, No. 9, pp 787 – 790, 2001
http://www.imm.ac.cn/journal/ccl.html

Two New Compounds from *Goniothalamus Cheliensis* Hu

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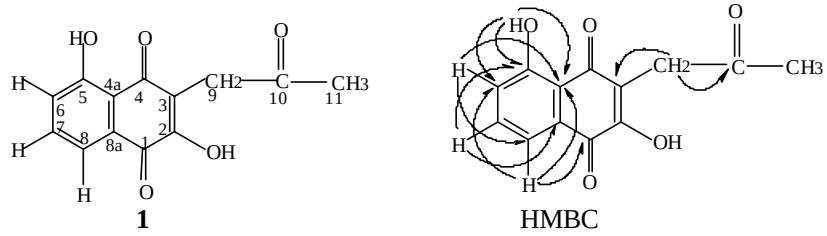
Abstract: Two new compounds, gonioquinone (**1**) and goniofufurone acetonide (**2**), have been isolated from the roots of *Goniothalamus cheliensis* Hu. Their structures were determined on the basis of spectral and chemical evidence.

Keywords: *Goniothalamus cheliensis* Hu, gonioquinone, goniofufurone acetonide.

Goniothalamus cheliensis Hu (Annonaceace) is a small tree or shrub in Yunnan Province, southwest of China. Acetogenins, styryllactones and alkaloids[1-3] from the genus were reported in the previous literature and many of them showed strong cytotoxic activities against a number of human cancer cell lines[4]. The titled plant has been the subject of our investigation due to the impressive cytotoxicity of its organic extract against mouse lymphocytic leukemia cells in preliminary pharmacological screening. Bioassy-guided fractionation of the EtOH extract of the roots resulted in the isolation of two new compounds, together with thirty-six known compounds. In this paper, we report the structure elucidation of the new compounds (**1** and **2**).

Figure 1 Structure and key HMBC correlations for **1**



1 HMBC

Gonioquinone (**1**) was isolated as orange needles, mp 201-202°C. Its molecular formula was determined as $C_{13}H_{10}O_5$ by HRFABMS at *m/z* 246.0907 $[M]^+$ (calcd. 246.0892).

The IR spectrum (KBr, cm^{-1}) displayed absorption bands for hydroxyl (3379), carbonyl (1685) and aromatic moiety (1616 and 1589). Its UV spectrum exhibited characteristic bands at λ_{max} (logε): 410 (3.73), 285 (4.19), 234 (4.24), and 210 (4.29) nm analogous to those of draserone and suggested that **1** had a naphthaquinone skeleton[5].

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The ^{1}H NMR spectrum of **1** showed the presence of two phenolic hydroxyl at δ 11.38 (s) and 10.07 (brs), three aromatic protons at δ 7. 75(d, 1H, *J*=8.0Hz), 7.74 (t, 1H, *J*=8.0Hz) and 7.20 (d, 1H, *J*=8.0Hz) and the absence of signals in the quinonoid proton region (δ 5.8-6.8) indicating **1** to be a 1,4-naphthoquinone substituted at the 2- and 3- positions[6]. The ^{13}C and DEPT NMR spectra displayed 13 carbon signals including one primary, one secondary, three tertiary and eight quarternary

Table 1 ^{1}H (500MHz) and ^{13}C (125MHz) NMR data of **1** in $CDCl_3$

Position	δ_H *J* (Hz)	δ_C	DEPT	Position	δ_H *J* (Hz)	δ_C	DEPT
1		180.4	s	7	7.74 t (8.0)	139.1	d
2	10.71brs	152.2	s	8	7.75 d (8.0)	119.7	d
3		109.2	s	8a		133.6	s
4		184.7	s	9	2.73 s	33.2	t
4a		113.9	s	10		202.2	s
5	11.38 s	161.8	s	11	1.25 s	29.7	q
6	7.20 d (8.0)	122.2	d				

Table 2 ^{1}H (500MHz) and ^{13}C(125MHz) NMR data of **2** in $CDCl_3$

Position	δ_H *J* (Hz)	δ_C	Position	δ_H *J* (Hz)	δ_C
2		174.5	10		101.8
3	2.71 d (3.0)	36.5	12	1.46 s	23.9
4	5.06 m	78.3	13	1.47 s	24.4
5	4.95 d (3.5)	87.0	1′		139.2
6	4.56 dd (8.0)	74.8	2′(6′)	7.41 m	126.3
7	4.44 dd (4.5, 8.0)	84.9	3′(5′)	7.36 m	128.5
8	4.65 d (4.5)	72.0	4′	7.31 m	128.0

carbons, which were identical with those of julomycin F except for the signal at δ 109.2 in the ^{13}C NMR spectrum suggesting that **1** had the same skeleton and substituted groups as julomycin F[7]. A combination of the ^{1}H and ^{13}C NMR spectra of **1** revealed the resonances for the protons at δ 2.73 (s, 2H) and 1.25 (s, 3H) and the carbons at δ 29.7, 202.2 and 33.2 indicating the presence of the fragment -CH_2COCH_3 (**Table 1**)[8]. The more shielded carbonyl resonance in the ^{13}C NMR spectrum was attributable to C-1 (δ 180.4) because of the existence of a electron-repelling phenolic hydroxyl in the vicinity of C-1[9].

Another hydroxyl was located at C-5 position, this finding was confirmed by the detailed analysis of J value and 2D NMR spectra. Three aromatic protons at δ 7.75, 7.74 and 7.20 with J values of 8.0Hz suggested that they were adjacent to each other. Combination with the HMQC spectrum, these protons were assigned to be connected with the carbons at δ 119.7 (C-8), 139.1 (C-7) and 122.2 (C-6) respectively. Furthermore, the HMBC correlations of the proton at δ_H 11.38 (OH) with the carbon signals at δ_C 161.8 （C-5） and 122.2（C-6） revealed that the phenolic hydroxyl was attached to C-5 position.

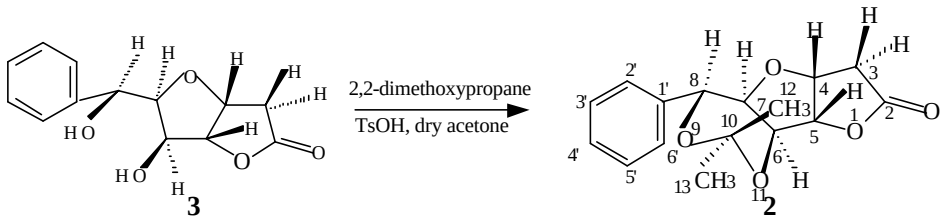
The left acetonyl was linked to C-3 position, it was determined by the HMBC correlations of the proton at δ_H 2.73 (H-9) with the carbon signals at δ_C 109.2 (C-3) and 202.2 (C-10). In the ^{13}C NMR spectrum, the signal for C-3 in **1** showed a more upfield

shift than C-3 of juglomycin F, it probably resulted from the formation of intramolecular hydrogen bond between the carbonyl group of C-4 and the phenolic hydroxyl proton of C-5[7].

Goniofufurone acetonide (**2**), mp 165-166°C, $[\alpha]_D^{23}$ +80 (c 0.05, MeOH), was obtained as white crystals. Its HRFABMS gave a quasi-molecular ion $[MH]^+$ at *m/z* 291.1248 (calcd. 291.1232), which fits the molecular formula $C_{16}H_{18}O_5$.

The IR spectrum (KBr, cm^{-1}) exhibited absorption bands for saturated γ-lactone (1786) and phenyl (1603 and 1495). Its ^1H NMR spectrum revealed the presence of five aromatic protons at δ 7.31-7.41 (m, 5H), five oxygenated methine protons at δ 4.44 -5.06, two methylene protons at δ 2.71 (d, 2H) and six methyl protons at δ 1.46 (s, 3H) and 1.47 (s, 3H) (**Table 2**), which were similar to those of goniofufurone (**3**) except for the signals of two methyl groups. By comparison of the ^{13}C NMR data with those of

Figure 2 Structures for **2** and goniofufrone (**3**)



goniofufurone, **2** had an additional signal at δ 101.8 and two additional methyl signals at δ 23.9 and 24.4, which suggested that **2** was acetone derivative of goniofufurone. This was confirmed by the preparation of **2** from **3** reacting with 2, 2-dimethoxyl propane, the derivative showed the same data of ^1H NMR and R_f value as **2**. So **2** has the same absolute configurations as goniofufurone namely 4R, 5S, 6R, 7R, 8R[10].

Acknowledgments

This research was supported by National 973 Project (G1998051120). The authors are grateful to the Department of Instrumental Analysis, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College for the measurements of UV, IR, NMR and MS spectra.

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Received 26 February, 2001