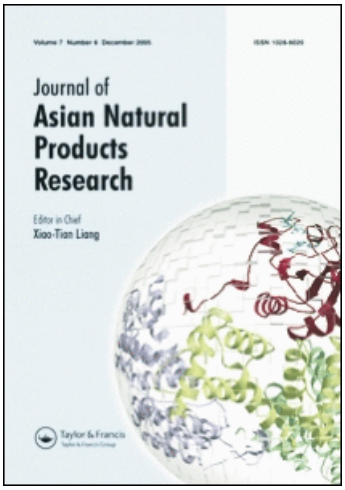


Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

Styryllactones from the Rhizomes of *Goniothalamus griffithii*

Yan Jun Zhang[a]; Guang Xiong Zhou[a]; Ruo Yun Chen[a]; De Quan Yu
[a] Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing, China

To cite this Article Zhang, Yan Jun , Zhou, Guang Xiong , Chen, Ruo Yun and Yu, De Quan(1999) 'Styryllactones from the Rhizomes of *Goniothalamus griffithii*', Journal of Asian Natural Products Research, 1: 3, 189 — 197
To link to this Article: DOI: 10.1080/10286029908039864
URL: http://dx.doi.org/10.1080/10286029908039864

JANPR, Vol. 1, pp. 189–197
Reprints available directly from the publisher
Photocopying permitted by license only

STYRYLLACTONES FROM THE RHIZOMES OF *GONIOTHALAMUS GRIFFITHII*

YAN JUN ZHANG, GUANG XIONG ZHOU,
RUO YUN CHEN and DE QUAN YU*

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

(Received 2 June 1998; Revised 20 June 1998; In final form 4 July 1998)

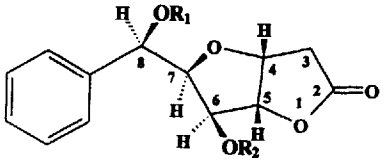
Three new styryl-lactones 8-acetylgoniofufurone(**1**), 7-acetylgonio-pypyrone(**3**), and 5-acetylgoniopypyrone(**4**), along with ten known compounds, goniofufurone(**2**), goniopypyrone(**5**), goniothalamin, goniothalenol, (+)-isoaltholactone, goniodiol, 7-acetylgoniodiol, goniotriol, 8-acetylgoniotriol, 9-deoxygoniopypyrone were isolated from the rhizomes of *Goniothalamus griffithii* Hook f. et. Thoms. Their structures were elucidated by IR, MS, NMR spectra and chemical evidence. All compounds showed cytotoxic activities against human cancer cell lines.

Keywords: Annonaceae; *Goniothalamus griffithii*; Styryllactone; 8-acetylgoniofurone; 7-acetylgoniopypyrone; 5-acetylgoniopypyrone

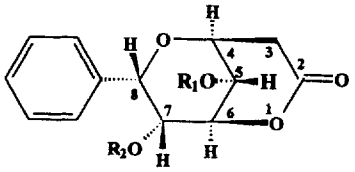
INTRODUCTION

Goniothalamus griffithii Hook f. et. Thoms is a small tree or shrub growing in Yunnan Province, Southwest part of China. The ethanolic extract of the rhizomes of *G. griffithii* was active against various human cancer cell lines. In our previous phytochemical study, the rhizomes of the plant were found to contain six phenanthrene lactam alkaloids and two anthraquinone alkaloids [1,2]. Further investigation on structurally new bioactive compounds from the rhizomes of *G. griffithii* have now resulted in the isolation of three new styryllactones, 8-acetylgoniofufurone(**1**), 7-acetylgoniopypyrone(**3**), and 5-acetylgoniopypyrone(**4**), as well as ten known styryllactones, goniofufurone(**2**) [4], goniopypyrone(**5**) [4], goniothalamin [6], goniothalenol [7],

* Corresponding author. Tel.: (010)63165224. E-mail: dquanyu@public.bta.net.cn.



1. R_1=Ac R_2=H 1a. R_1=R_2=Ac
2. R_1=R_2=H



3. R_1=H R_2=Ac 3a. R_1=R_2=Ac
4. R_1=Ac R_2=H 5. R_1=R_2=H

FIGURE 1 The structures of **1**–**5**.

(+)-isoaltholactone [8], goniodiol [9], 7-acetyl-goniodiol [10], goniotriol [11], 8-acetylgoniotriol [4], and 9-deoxygoniopypyrone [12]. Their structures were elucidated by IR, MS, ^{1}H-NMR, ^{13}C-NMR and ^{1}H–^{1}H COSY,^{13}C–^{1}H COSY spectra, and the relative configurations were determined by comparison of the NMR and $[\alpha]$ values with those of known compounds as well as chemical evidence. The absolute configurations of **1** and **3** (Fig. 1) were confirmed on the basis of Mosher's methodology [3] by comparison of the NMR data of (R-) and (S-)-MTPA derivatives of **1** and **3**.

RESULTS AND DISCUSSION

8-Acetylgoniofufurone(**1**) was obtained as white needles. The HREIMS of **1** gave *m/z* 292.0946 for [M^+] corresponding to the molecular formula $C_{15}H_{16}O_6$ (calcd. 292.0947). The presence of a hydroxyl group was indicated by the peak at *m/z* 274 [$M-H_2O$]$^+$ in EIMS and a sharp hydroxyl band at 3537 cm^{-1} in the IR spectrum of **1**. Two carbonyl peaks at 1766 and 1728 cm^{-1} represented a saturated γ-lactone and an ester carbonyl. A singlet at δ2.14(3H, s) in the ^{1}H-NMR spectrum of **1** indicated the presence of an acetoxyl group. Therefore, the structure contained a hydroxyl and an acetoxyl group.

The ^{13}C-NMR spectrum of **1** showed the presence of 15 carbons (Table I). Two lowfield peaks (δ_c175.19 and 171.68) were assigned to the saturated γ-lactone carbonyl carbon and acetyl carbonyl carbon, four peaks at δ_c136.57(C-1′), 128.62 (C-3′, 5′), 127.63 (C-2′, 6′), and 128.95 (C-4′) indicated the presence of a monosubstituted phenyl; also five carbons linked to oxygen and a methylene carbon as well as a methyl carbon were observed. The ^{1}H-NMR spectrum of **1** (Table II) showed the presence of five phenyl protons at δ7.36–7.40 and five oxygenated methine protons at δ4.16–5.88,

TABLE I ^{13}C-NMR data of compounds **1**–**5**(125 MHz, $CDCl_3$)

Carbon	**1**	**2**	**3**	**4**	**5**
2	175.19	175.18	167.07	166.92	167.79
3	35.75	35.06	34.96	35.24	35.17
4	77.00	77.33	70.86	68.15	70.93
5	86.97	87.45	63.99	65.41	64.48
6	73.23	74.57	71.81	71.91	72.66
7	82.23	83.01	69.16	68.95	70.35
8	72.97	73.57	69.26	70.39	70.14
1′	136.57	138.93	135.52	136.30	135.90
2′,6′	127.63	125.89	126.07	126.03	126.19
3′,5′	128.62	128.63	128.33	128.54	129.01
4′	128.95	128.50	128.33	128.13	128.63
OAc	171.68		168.00	169.22	
CH_3	21.17		20.25	20.87	

two methylene protons at δ2.65, 2.54, and a methyl group at δ2.14(3H, s). These NMR data were quite similar to those of goniofufurone(**2**) except for the presence of an acetyl group in **1**.

The ^{1}H-NMR and ^{1}H–^{1}H COSY spectra of **1** showed that the two methylene protons (3-H_a and 3-H_b) and 4-H formed a simplified ABX system. Examination of the Dreiding molecular model and coupling constant $J_{4/5}$ (4.1 Hz) showed that 4-H and 5-H should be in *cis* configuration; the dihedral angle between 4-H and 5-H is close to 0°; The coupling between 5-H and 6-H was not observed in the ^{1}H-NMR spectrum of **1** which indicated that 5-H and 6-H should be in *trans* configuration with a dihedral angle close to 90° as shown by the Dreiding molecular model. The $J_{6/7}$ value (2.2 Hz) indicated that 7-H was in *cis* relationship with 6-H. The formation of an intramolecular hydrogen bond between C_6-OH and C_8-$OCOCH_3$ in **1** indicated in a relative *cis* configuration for 6-H and 7-H. Comparing the NMR data of **1** with those of goniofufurone(**2**) showed that the chemical shift of 8-H was obviously moved downfield by 0.69 ppm, therefore the acetyl was linked to C-8. The coupling constant of 7-H and 8-H showed a significant change from 4.8 Hz (**2**) to 9.0 Hz (**1**). This suggested that the intramolecular hydrogen bond may be distorted, and the dihedral angle between 7-H and 8-H could change when the hydroxyl at C-8 was replaced by an acetoxyl group.

Hydrolysis of **1** with hydrochloric acid yielded goniofufurone(**2**). Its mp, MS, NMR and [α] were identical with those reported in literatures [4,5]. Acetylation of **1** yielded a compound identical with diacetylgoniofufurone [4] Thus, the structure of **1** was determined as 8-acetylgoniofufurone. (R-) and (S-)-MTPA ester of **1** was prepared to confirm its absolute configuration. The $\Delta\delta_{s-r}$ values of 3-H, 4-H, 5-H, 7-H, 8-H were +0.04, +0.16, +0.15, 0, −0.02,

TABLE II ^{1}H-NMR data of compounds **1**–**5**(500 MHz, $CDCl_3$)

Protons	**1**	**2**	**3**	**4**	**5**
H-3a	2.65, dd, (19.7, 5.7 Hz)	2.75, dd, (18.7, 5.8 Hz)	3.14, dd, (19.6, 1.5 Hz)	3.10, brs	3.08, dd, (19.5, 1.6 Hz)
H-3b	2.54, d, (19.7 Hz)	2.68, d, (18.7 Hz)	3.07, dd, (19.6, 5.2 Hz)		3.00, dd, (19.5, 5.0 Hz)
H-4	4.96, dd, (5.7, 4.1 Hz)	5.11, dd, (5.8, 4.2 Hz)	4.50, m, (5.2, 1.5, 2.8 Hz)	4.55, brs	4.46, m, (5.0, 1.8, 1.6 Hz)
H-5	4.97, brd, (4.1 Hz)	4.86, brd, (4.2 Hz)	4.03, m, (2.8, 3.6 Hz)	5.14, brs	4.02, dd, (3.7, 1.8 Hz)
H-6	4.37, brd, (2.2 Hz)	4.40, brd, (2.6 Hz)	4.68, brdd, (6.1, 3.6 Hz)	4.84, brs	4.80, dd, (6.1, 3.7 Hz)
H-7	4.16, dd, (9.0, 2.2 Hz)	4.09, dd, (2.6, 4.8 Hz)	5.38, dd, (6.1, 2.1 Hz)	4.06, brs	4.12, dd, (6.1, 1.9 Hz)
H-8	5.88, d, (9.0 Hz)	5.19, d, (4.8 Hz)	5.11, d, (2.1 Hz)	5.04, brs	5.01, d (1.9 Hz)
OAc	2.14, s		1.82, s	2.20, s	
Ar–H	7.36–7.40	7.33–7.44	7.29–7.37	7.32–7.42	7.35–7.45

respectively. According to Mosher's assumption [3], only R configuration of C-6 could have greater shielding of 3-H, 4-H, 5-H, and less shielding of 7-H, 8-H in the (R-)-MTPA derivatives of **1**. Therefore, the structure of **1** should have the absolute configuration of 4R, 5S, 6R, 7R, 8R.

7-Acetylgoniopypyrone was obtained as white needles. The HREIMS of **3** showed a molecular ion at *m/z* 292.0951 corresponding to the molecular formula $C_{15}H_{16}O_6$ (calcd.: 292.0947). Hydroxyl absorption band at 3572 cm^{-1} and carbonyl absorption bands at 1744, 1739 cm^{-1} were present in the IR spectrum of **3** and two carbonyl groups were confirmed by the small peaks at δ_c 168.20, 167.07 ppm in the ^{13}C-NMR spectrum of **3**. The ^{1}H-NMR spectrum of **3** showed a monosubstituted phenyl moiety, five oxygenated methine protons, a methylene and a methyl group. ^{13}C-NMR spectrum of **3** showed the presence of 15 carbons including a monosubstituted phenyl moiety, two carbonyls, five oxygenated methine carbons, a methylene carbon, and a methyl carbon. These data were quite similar to those of goniopypyrone(**5**) except for the presence of an acetyl group in **3**. It indicated that **3** has the same skeleton as **5**. All the oxygenated methine protons were assigned based on the ^{1}H–^{1}H COSY spectrum of **3**. The chemical shift of 7-H obviously moved downfield by 1.36 ppm compared to that of **5**. So, the acetyl should be linked to C-7, the hydroxyl to C-5.

Examination of the Dreiding molecular model and coupling constant of $J_{4/5}$ indicated that the dihedral angle of 4-H and 5-H was close to 90°. The two methylene protons 3-H_a, 3-H_b and 4-H formed a simplified ABX system. Esterification of 5-OH may affect the chemical shift of 3-H and the coupling constant between 3-H_a, 3-H_b and 4-H. This may happen when 4-H and 5-H, 5-H and 6-H, as well as 6-H and 7-H were in *trans* configuration.

5-Acetylgoniopypyrone was obtained as a white solid. The HREIMS of **4** gave a $[M]^+$ at *m/z* 292.0946 compatible with $C_{15}H_{16}O_6$ (calcd. 292.0947). Its spectral data were quite similar to those of **3**. Hydroxyl absorption band at 3489 cm^{-1} and carbonyl absorption bands at 1737, 1729 cm^{-1} were present in the IR spectrum of **4** and two carbonyl groups were confirmed by the peaks at δ_c169.22, 166.92 in the ^{13}C-NMR spectrum of **4**. The ^{1}H-NMR spectrum of **4** also showed the presence of a monosubstituted phenyl moiety, five oxygenated methine protons, a methylene and a methyl group. ^{13}C-NMR spectrum of **4** showed the presence of 15 carbons including a monosubstituted phenyl moiety, two carbonyls, five oxygenated methine carbons, a methylene carbon, and a methyl carbon as well. All the oxygenated methine protons were assigned based on the ^{1}H–^{1}H COSY spectrum of **4**. The main difference between **4** and **3** is that the chemical shift of 5-H in **4** and 7-H in **3** were obviously moved downfield by more than 1 ppm

TABLE III Bioactivity* of compounds **1–5**

Compounds	IC_{50} (mol/L)			
	A2780	HCT-8	KB	MCF-7
1	2.53×10^{-5}	3.20×10^{-6}	4.41×10^{-5}	–
2	1.00×10^{-4}	1.00×10^{-4}	1.00×10^{-4}	1.00×10^{-4}
3	1.00×10^{-4}	1.00×10^{-4}	1.00×10^{-4}	—
4	1.63×10^{-5}	1.08×10^{-5}	2.53×10^{-5}	1.34×10^{-5}
5	1.00×10^{-4}	2.58×10^{-5}	1.00×10^{-4}	—

*All data were measured in MTT method.

compared to that of **5**. So, the acetyl should be linked to C-5, the hydroxyl to C-7.

Acetylation of **3** and **4** yielded the same compound identical with diacetylgoniopypyrone(**3a**) [4]. So the relative configurations of **3** and **4** were identical with that of goniopypyrone(**5**). (R-) and (S-) MTPA ester derivatives were prepared to confirm the absolute configuration of **3**. The $\Delta\delta_{S-R}$ values of 3-H, 4-H, 6-H and 7-H were −0.03, −0.15, +0.10 and +0.03, respectively. According to Mosher's assumption [3] only S configuration of C-5 could have greater shielding of 6-H, 7-H, and less shielding of 3-H, 4-H in the (S-)-MTPA derivatives of **3**. Therefore, the structure of **3** should have the absolute configuration of 4S, 5S, 6R, 7R, 8S.

Compound **1–5** showed cytotoxic activity against various human cancer cell lines (A 2780, HCT-8, KB, MCF-7) (Table III).

EXPERIMENTAL SECTION

General Experimental Procedure

Melting points were determined on a micro-melting point apparatus and are uncorrected. IR spectra (KBr) were measured on a Perkin-Elmer 683 infrared spectrometer. Optical rotations were taken on a Perkin-Elmer 241 polarimeter. ^1H and ^{13}C-NMR along with ^1H–^1H COSY, ^{13}C–^1H COSY spectra were obtained on a Bruker AM 500 spectrometer in $CDCl_3$. EIMS and HREIMS data were recorded on a ZAB-2F and a Zebspec spectrometer. UV spectra were run on a Shimadzu UV-240 spectrometer. [+]- and [−]-MTPA were the products of Sigma Chemical Co.

Plant Material

The plant material (roots) was collected from Jinghong County, Yunnan Province, China, in July 1996, and identified as *G. griffithii* Hook. F. et.

Thoms by Professor Shao Rong Guo, Institute of Medicinal Plant Development, Chinese Academy of Medical Sciences, where a voucher specimen (96021) of the plant is deposited.

Extraction and Isolation

The dried roots (9.1 kg) of *G. griffithii* were exhaustively extracted with 95% ethanol and evaporated *in vacuo* to yield extract F_1 (1000 g) which was partitioned between H_2O and $CHCl_3$ (1 : 1) giving a water soluble fraction F_2 (310 g) and a $CHCl_3$ soluble fraction F_3 (373 g) as well as an insoluble fraction F_6 (320 g).The $CHCl_3$ soluble fraction F_3 was first dissolved in 90% methanol and defatted with petroleum ether to give methanol soluble fraction F_4 (268 g). F_4 was subjected to column chromatography on silica gel (160–200 mesh) and eluted with petroleum ether : acetone gradients. 60 fractions(FB) and 120 fractions(FC), each 250 ml, eluted by petroleum ether–acetone 8 : 2 and 6 : 4 were collected. From FB17-58 goniothalenol (23.5 g) was obtained. The residue of this fraction was subjected to column chromatography on silica gel and eluted with petroleum ether–ethyl acetate (7 : 3), (+)isoalthalactone (324 mg), 7-acetyl-goniodiol (310 mg), and gonio-thalamin (5.32 g) were obtained. FB were subjected to chromatography on silica gel repeatedly to afford 5-acetyl-goniopypyrone(**4**, 063 mg), 9-deoxygoniopypyrone (39 mg), 7-acetylgoniopypyrone(**3**, 110 mg), 8-acetylgoniofufurone(**1**, 267 mg), goniofufurone(**2**, 230 mg), goniopypyrone(**5**, 170 mg), 8-acetylgoniotriol (125 mg), goniodiol (3.50 g), and goniotriol (37 mg).

8-Acetylgoniofufurone (**1**) white needles from MeOH, 267 mg, mp 176–178°C, $[\alpha]_D^{24}$ +26.5(c0.05 EtOH); UV (MeOH) λ_{max} 213, 255 nm; IR (KBr) ν_{max} 3537(OH), 2885, 1766(lactone C=O), 1728(ester), 1381(CH), 1240, 1043, 700, 551 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) and ^{13}C-NMR (125 MHz, $CDCl_3$) see Tables I and II; EIMS *m/z* 292$[M]^+$ (0.6) 274(0.1), 232(4.3), 191(78), 126(35.2), 107(100), 92 (36.1), 82(34.0); HREIMS *m/z* 292.0946, cacld. for $C_{15}H_{16}O_6$, 292.0947.

(R-) *and* (S-) *MTPA derivatives of* **1** 16 mg 8-acetylgoniofufurone(**1**) was dissolved in 2 ml dry CH_2Cl_2, divided into two parts, and treated with (R-) and (S-)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA) respectively in the presence of DCC and DMAP at room temperature overnight. The (R-) and (S-)-MTPA derivatives of **1** were purified by preparative TLC on silica gel eluting with petroleum ether–ethyl acetate (3 : 2). ^{1}H-NMR (500 MHz, $CDCl_3$) are shown in Table IV.

TABLE IV $\Delta\delta_{S-R}$ data of MTPA derivatives of **1** and **3**(500 MHz, $CDCl_3$)

Protons	**1**			**3**		
	δ_S	δ_R	$\Delta\delta_{S-R}$	δ_S	δ_R	$\Delta\delta_{S-R}$
3-H	2.62	2.58	+0.04	3.17	3.20	−0.03
4-H	4.92	4.76	+0.16	4.69	4.84	−0.15
5-H	4.86	4.71	+0.15	5.27	5.24	
6-H	5.77	5.81		4.85	4.74	+0.11
7-H	4.46	4.46	0	5.17	5.14	+0.03
8-H	5.54	5.56	−0.02	5.04	5.14	
8-OAc	1.96	2.02				
7-OAc				1.51	1.41	

Diacetylgoniofufurone (**1a**) 8-acetylgoniofufurone(**1**, 10 mg) was dissolved in 0.5 ml pyridine and treated with 0.5 ml Ac_2O at room temperature overnight. The usual work-up gave a solid (11 mg). The solid was dissolved in acetone and subjected to preparative TLC on silica gel eluting with petroleum–ethyl acetate (3 : 2) and afforded 7 mg diacetylgoniofufurone(**1a**). Goniofufurone(**2**) was acetylated by the same method as **1**. The diacetylgoniofufurone(**1a**) obtained from **1** and **2** has the same chemical and physical property (mp 132–134°C and same R_f). ^{1}H-NMR (500 MHz, $CDCl_3$) 7.26–7.38 (5H, m, Ar–H), 5.84 (1H, d, J = 9.48 Hz, 8-H), 5.73(1H, brd, J = 3.16 Hz, 6-H), 4.98(1H, dd, J = 4.44, 5.31 Hz, 4-H), 4.87(1H, brd, J = 4.44 Hz, 5-H), 4.46(1H, dd, J = 9.48, 3.16 Hz, 7-H), 2.69(1H, dd, J = 18.86, 5.31 Hz, 3-Ha), 2.59(1H, d, J = 18.86 Hz, 3-Hb), 2.13(3H, sOAc), 2.00(3H, s, OAc).

Hydrolysis of 8-acetylgoniofufurone (**1**) 8-Acetylgoniofufurone (**1**, 16 mg) dissolved in 1 ml MeOH and 0.2 ml 1N hydrochloric acid was allowed to stand at room temperature overnight, and neutralized with Na_2CO_3 solution. The reaction mixture was evaporated *in vacuo* to yield a residue. The residue was subjected to preparative TLC on silica gel to afford goniofufurone (**2**, 6 mg).

7-Acetylgoniopypyrone (**3**) white needles from acetone, 110 mg, mp 140–142°C; $[\alpha]_D^{24}$ +8.8(c0.06, EtOH); UV (MeOH) λ_{max} 210, 255 nm; IR (KBr) ν_{max} 3572(OH), 2918, 1742(lactone), 1739(ester), 1363, 1217, 1059 cm^{-1}; ^{1}H-NMR(500 MHz, $CDCl_3$) and ^{13}C–NMR (125 MHz, $CDCl_3$) see Tables I and II; EIMS *m/z* 292(12), 274(0.5), 231(25), 188(19), 107(100), 91(31), 79(47), 57(43); HREIMS *m/z* 292.0951, cacld. for $C_{15}H_{16}O_6$, 292.0947.

(R-) *and* (S-) *MTPA derivatives of* **3** 18 mg 7-acetylgoniopypyrone(**3**) was treated by the same procedure as **1**. The (R-) and (S-)-MTPA derivatives of **3** were purified by preparative TLC on silica gel eluting with

petroleum ether–ethyl acetate (3 : 2). ^{1}H-NMR (500 MHz, $CDCl_3$) are shown in Table IV.

Diacetylgoniopypyrone (**3a**) Acetylation of 7-acetylgoniopypyrone(**3**), 5-acetyl-goniopypyrone(**4**), and goniopypyrone(**5**) by the same method as **1** gave the title compound. White needles, mp 156–158°C; ^{1}H-NMR (500 MHz, $CDCl_3$) 7.33–7.41 (5H, m, Ar–H), 5.26 (1H, dd, $J = 2.49$, 3.29 Hz, 7-H), 5.08(1H, d, $J = 2.49$ Hz, 8-H), 5.02(1H, dd, $J = 1.22$, 3.21 Hz, 5-H), 4.85(1H, dd, $J = 3.21$, 3.29 Hz, 6-H), 4.59(1H, dd, $J = 3.50$, 1.22 Hz, 4-H), 3.12(2H, d, $J = 3.50$ Hz, 3-H). 2.20(3H, s, OAc), 1.79(3H, s, OAC).

5-Acetylgoniopypyrone (**4**) white solids from MeOH, 63 mg, mp 194–196°C; $[\alpha]_D^{24}$ +30(c 0.5 EtOH); UV (MeOH) λ_{max} 209, 255, 285 nm; IR (KBr) ν_{max} 3489 (OH), 1731, 1720, 1263, 1057 cm^{-1}; ^{1}H-NMR (500 MHz,$CDCl_3$) and ^{13}C-NMR (125 MHz, $CDCl_3$) see Tables I and II; EIMS *m/z* 292(5.5), 274(19.9), 188(24), 187(27), 173(26), 143(22), 107(100), 97(50), 91(60), 79(41), 57(43); HREIMS *m/z* 292.0946, cacld. for $C_{15}H_{16}O_6$, 292.0947.

Acknowledgment

This work was supported by the Science Foundation of Chinese Academy of Medical Sciences. The authors thank Professor Shao-rong Guo for the plant material identification; Professor Man Kong and Wen-yi He for NMR measurements.

References

[1] Y.J. Zhang, R.Y. Chen and D.Q. Yu *Phytochemistry* 1998 (in press).
[2] Y.J. Zhang, M. Kong, R.Y. Chen and D.Q. Yu *Chinese Chemical Letters* 1998 (in press).
[3] T. ohtani, T. Kusumi, Y. Kashman and H. Kakisawa *J.* Am. Chem. Soc. 1991, **113**, 4092–4096.
[4] X.P. Fang, J.E. Anderson, C.J. Chang, P.E. Fannwick and J.L. McLaughlin *J. Chem. Soc. Perkin Trans.* 1990, 1655–1661.
[5] J.P. Surivet and J.M. Vatele *Tetrahadron Letters* 1996, **37**(25), 4373–4376.
[6] K. Jewers, J.B. Davis, J. Dougan, A.H. manchnda, G. Blunden, A. Kyi and S. Wetchapian *Phytochemistry* 1972, **11**, 2025.
[7] A.A. Ebrahim El-Zayat, N.R. Ferrigni, T.G. McLoud, A.T. McKenzie, S.R. Byrn, J.M. Cassady, C.J. Chang and J.L. McLaughlin *Tetrahedron Letters* 1985, **26**, 955–956.
[8] S.M. Colegte, L.B. Din, A. Latiff, K.M. Salleh, M.W. Samsudin, B.W. Skelton, K.I. Tadano, A.H. White and Z. Zakaric *Phytochemistry* 1990, **29**, 1701–1704.
[9] S.K. Talapatra, D. Basu, S. Goswami and B. Talapatra *Indian J. Chem.* 1985, **24B**, 29–34.
[10] Y.C. Wu, C.Y. Duh, F.R. Chang, G.Y. Chang and K.H. Lee *J. Nat. Prod.* 1991, **54**, 1077–1081.
[11] A. Alkofahi, W.W. Ma, A.T. McKenzie, S.R. Byrn, J.L. McLaughlin *J. Nat. Prod.* 1989, **52**, 1371–1373.
[12] X.P. Fang, J.E. Anderson, C.J. Chang and J.L. McLaughlin *J. Nat. Prod.* 1991, **54**, 1034–1043.