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Three New Styrylpyrones from *Goniothalamus leiocarpus*

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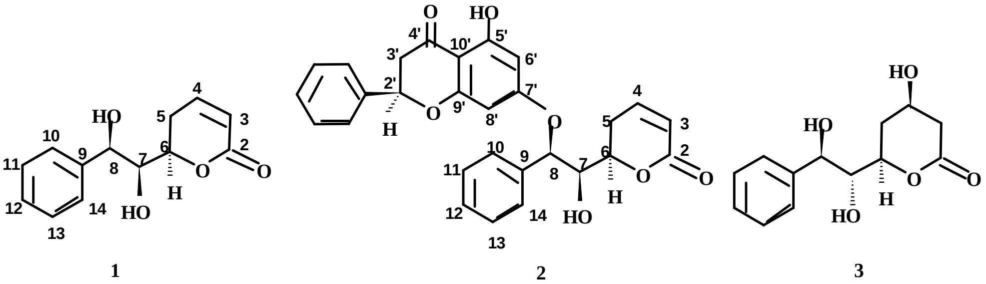
Abstract: Three new styrylpyrones, named 7-*epi*-goniodiol **1**, leiocarpin B **2** and leiocarpin C **3**, were isolated from the stem barks of *Goniothalamus leiocarpus*. Their structures were elucidated by means of spectral and chemical methods. The relative configuration of **1** and **2** were determined by X-ray crystallographic analysis.

Keywords: Annonaceae; *Goniothalamus leiocarpus*; styrylpyrone; 7-*epi*-goniodiol; leiocarpin B; leiocarpin C.

Goniothalamus leiocarpus (Annonaceae family) is a tropical plant distributed in south of Yunnan province of China. We have isolated a new styrylpypyrone--leiocarpin A[1] from the stem barks of *Goniothalamus leiocarpus* and four known annonaceous acetogenins[2] from the seeds of the same plant. In this paper, we reported three new styrylpyrones, named 7-*epi*-goniodiol **1**, leiocarpin B **2** and leiocarpin C **3** respectively. They were isolated from the ethanolic extract of stem barks of the plant by repeatedly chromatography of silica columns. Their structures were elucidated by means of spectral and chemical methods. The relative configuration of **1** and **2** were determined by X-ray crystallographic analysis.

Figure 1. Stuctures of **1**, **2** and **3**



1 **2** **3**

Compound **1** $[\alpha]_D^{20}$ +96.4（CHCl$_3$, c 0.3）. The molecular weight was suggested by a prominent peak at m/z 235 $[MH]^+$ in the FABMS spectrum. The presence of two hydroxyl groups were indicated by peaks at m/z 217 $[MH\text{-}H_2O]^+$ and 199 $[MH\text{-}2H_2O]^+$ in the FABMS as well. The hydroxyl groups at 3500 cm^{-1} and α,β-unsaturated δ-lactone bands at 1626 and 1705 cm^{-1} were presented in the IR spectrum. The molecular formula $C_{13}H_{14}O_4$ and planar structure, which were the same as a known styrylpyrone compound -- goniodiol[3], were given by the data of ^{1}H and ^{13}C NMR spectra of **1**. Whereas the careful examination of the ^{1}H NMR gave distinct differences of H-6, H-7 and H-8 either in chemical shifts or in coupling constants between **1** and goniodiol. The coupling constants of H-6/H-7 and H-7/H-8 in **1** were 5.8 and 3.7 Hz, while those in goniodiol were reported to be 2.2 and 7.0 Hz (*6,7-threo* and 7,8-*erythro*) respectively. This means there were distinction of configuration in H-6, H-7 and H-8 between goniodiol and **1**. Finally, the relative configuration of **1** was established as 6,7-*erythro* and 7,8-*threo* or 6R*, 7S* and 8R* by comparison of coupling constants and crystallographic analysis of X-ray [6], and **1** was therefore determined as 7-*epi*-goniodiol.

Table 1 NMR Data of Compound **1** and **3**
(^{1}H NMR 400 MHz and ^{13}C NMR 100 MHz, δ, ppm; J, Hz, in C_5D_5N,)

Compound	**1**		**3**	
Position	H	C	H	C
2	----	164.16	----	174.34
3	6.95 ddd, 9.8,1.6, 0.8	121.13	3.48 dd, 15.4, 8.9; 3.13 dd, 15.4, 5.4	41.20
4	6.82 ddd, 9.7, 5.8, 2.7	146.55	4.79 m$^+$	69.17
5	2.78 ddt, 18.7, 10.9, 2.6; 2.71 ddd, 18.7, 5.8, 4.8	25.93	2.43 ddd, 13.2, 6.8, 6.6; 2.17 dd, 13.2, 4.2	35.54
6	4.90 ddd, 10.9, 5.8, 5.0	78.62	4.39 dt, 7.5, 3.6	67.64
7	4.30 dd, 5.9, 3.7	72.81	4.68 dd, 5.8, 2.9	71.77
8	5.39 d, 3.7	76.95	5.51 d, 5.8	74.96
9	----	144.25	----	141.15
10, 14	7.74 d, 7.2	127.49	7.79 d, 7.6	127.95
11, 13	7.39 d, 7.3	128.62	7.35 d, 7.6	128.64
12	7.29 t, 7.3	127.57	7.25 t, 7.3	127.54

$^+$ only J=5.4 Hz (a double peak) could be measured in the ^{1}H NMR specrtum.

Leiocarpin B **2** was colorless needle, mp 189-191°C, $[\alpha]_D^{24}$ +28.8 (c 0.52 in CHCl$_3$) . The IR spectrum of **2** presented a hydroxyl band at 3500 cm^{-1} and the carbonyl peak of a unsaturated δ-lactone at 1700 cm^{-1}. The ^{13}C NMR showed the existence of 28 carbons (**Table 2**), which were respectively attributed to two structural units: 7-*epi*-goniodiol and pinocembrin (5,7-dihydroxy-dihydroflavone); two mono-substituted phenyls and the other 12 protons were also respectively corresponded to the above two structures in the ^{1}H and ^{13}C NMR. The molecular weight of **2** was indicated by a prominent peak at m/z 472 in the EIMS spectrum, and the molecular formula $C_{28}H_{24}O_7$ was determined by the peak at m/z 472.1536 (calcd. 472.1552) in the HREIMS. The structure of **2** was established as **Figure 1** by the spectra of ^{1}H-^{1}H COSY, HECTOR and NOESY. 7'-O-5'-hydroxydihydroflavone group positioned at C-8 of **2**, that was suggested by the long-range coupling signal between H-8 and C-7' in the COLOC spectrum of **2**. This structure was confirmed by X-ray crystallographic analysis[6].

Table 2 NMR Spectral Data of Leiocrpin B **2**
(^{1}H NMR 400 MHz and ^{13}C NMR100 MHz, δ, ppm; J, Hz, in C_5D_5N)

No.	H	C	No.	H	C
2	----	163.65	3'	3.12 dd, 17.1, 13.2; 2.78 dd, 17.1, 3.2	43.42
3	6.10 dd, 9.8, 1.8	121.17	4'	----	196.41
4	6.93 ddd, 9.8, 2.6, 1.7	146.17	5'	----	164.47
5	2.17 dt, 13.2, 6.7; 2.77 ddd, 18.9, 13.2, 2.6	26.21	6'	4.39 d, 2.3	97.62
6	4.96 ddd, 6.8, 4.6, 4.4	77.94	7'	----	167.04
7	4.38 dd, 6.8, 3.2	75.76	8'	4.48 d, 2.3	95.91
8	6.01 d, 3.2	80.01	9'	----	163.42
9	----	138.82	10'	----	103.85
10, 14	7.25-7.70 m	127.64	1"	----	139.30
11, 13	7.25-7.70 m	129.10	2", 6"	7.25-7.70 m	126.83
12	7.25-7.70 m	128.49	3", 5"	7.25-7.70 m	129.10
2'	5.34 dd, 13.2, 3.0	79.52	4"	7.25-7.70 m	129.04

Leiocarpin C **3** was isolated as needle, mp 131-132℃, $[\alpha]^{24}_{D}$ -63.9 (c 0.46, $CHCl_3$). The molecular weight of **3** was indicated by a prominent peak at m/z 253 $[MH]^+$ in the FABMS and a peak at m/z 252 $[M]^+$ in the EIMS. The HRFABMS gave m/z 253.0984 (calcd. 253.1076) for MH^+ of **3**, corresponding to the molecular formula $C_{13}H_{16}O_5$. The presence of three hydroxyl groups were indicated by peaks at m/z 235 $[MH\text{-}H_2O]^+$, 217 $[MH\text{-}2H_2O]^+$, 199 $[MH\text{-}3H_2O]^+$ in the EIMS and 234 $[M\text{-}H_2O]^+$, 216 $[M\text{-}2H_2O]^+$, 198 $[M\text{-}3H_2O]^+$, and by two absorption bands at 3400 and 3260 cm^{-1} in the IR spectrum. The existence of a saturated δ-lactone was supported by carbonyl bands at 1710 and 1690cm^{-1} in the IR spectrum. By analyzing of the ^{1}H NMR spectral data (**Table 1**), the molecular structure of **3** was established as 6-(7,8-dihydro-7,8-dihdroxystyryl)-3,4,5,6-tetrahydro-4-hydroxy-2-pyrone (**Figure 1**).

The relative configuration C-6, C-7 and C-8 of **3** could be determined by careful examination of coupling constants between H-6 and H-7, H-7 and H-8[4,5]. The coupling constants H-6/H-7 and H-7/H-8 in goniodiol were reported to be 2.2 and 7.0 Hz (6,7-*threo*-7,8-*erythro*)[3]. In compound **3**, the constants H-6/H-7 and H-7/H-8 were observed to be 2.9 and 5.8 Hz, respectively. So, the relative configuration of H-6/H-7 and H-7/H-8 in **3** agreed with that of goniodiol, and was determined as 6,7-*erythro* and 7,8-*threo*.

In the NOE spectrum of **3**, the presence of correlation of Ph-H/H_2-3, Ph-H/H_2-5, and the absence of correlation of Ph-H/H-6, Ph-H/H-4 suggested that H-6 and H-4 positioned on the same plane. Since H-6 was arranged in α-orientation in the determined configuration (6,7-*erythro*-7,8-*threo*), H-4 was therefore assigned on α-orientation. That was to say, the hydroxyl group at C-4 was identical as 4β-OH. Thus, the relative configuration of leiocarpin C **3** were determined as 6,7-*erythro*-7,8-*threo* and 4β-OH.

Acknowledgments

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References and Notes

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6 Crystallographic parameters of **1** and **2** have been deposited in the editorial office of CCL.

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