

## FOUR NEW STYRYLLACTONES FROM *GONIOTHALAMUS LEIOCARPUS*

Qing Mu, Weidong Tang,<sup>+</sup> Chaoming Li,<sup>\*</sup> Yang Lu,<sup>\*\*</sup> Handong Sun, Huilan Zheng, Xiaojiang Hao, Qitai Zheng,<sup>\*\*</sup> Nan Wu,<sup>\*\*</sup> Liguang Lou,<sup>+</sup> and Bin Xu<sup>+</sup>

Phytochemistry Laboratory, Kunming Institute of Botany, the Chinese Academy of Sciences, Kunming 650204, China <sup>+</sup>Shanghai Institute of Medical Material, the Chinese Academy of Sciences, Shanghai 200032, China <sup>\*\*</sup>Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050, China

**Abstract** – Four new styryllactones, leiocarpin A (**1**), 7-*epi*-goniodiol (**2**), leiocarpin B (**3**) and leiocarpin C (**4**), respectively, were isolated from the stem bark of *Goniothalamus leiocarpus*. Their structures were elucidated by means of spectral method. The relative configurations of **1**, **2** and **3** were determined by X-Ray crystallographic analysis. Compounds **2** and **3** possess antitumor activities.

*Goniothalamus leiocarpus* (Annonaceae family) is a tropical plant distributed in south of Yunnan province in China. We have isolated four known annonaceous acetogenins<sup>1</sup> from the seeds of *Goniothalamus leiocarpus*. In this paper, we report four styryllactones, named leiocarpin A (**1**), 7-*epi*-goniodiol (**2**), leiocarpin B (**3**) and leiocarpin C (**4**), respectively, isolated from the ethanolic extract of stem barks of the plant by repeat chromatography over silica gel. Their structures were elucidated by means of spectral. The relative configurations of **1**, **2** and **3** were determined by X-Ray crystallographic analysis. Compounds (**2**) and (**3**) showed activities in *vitro* anticancer test.

Leiocarpin A (**1**) was isolated as crystal, mp 132-134°C,  $[\alpha]_D^{24}$  -98.4° (c 0.60 in CHCl<sub>3</sub>). IR spectrum indicated the presence of a δ-lactone (1720 cm<sup>-1</sup>) and a hydroxyl (3360 cm<sup>-1</sup>) groups. <sup>1</sup>H and <sup>13</sup>C NMR spectra<sup>2</sup> showed that **1** had a phenyl (δ 7.25-7.43 ppm, 5H, m), four oxymethines (δ 65.62, 72.27, 73.92, and 76.38 ppm) and two methylenes (δ 29.58 and 36.35 ppm). These spectral data suggested that **1** was a styryllactone. The same molecular formula C<sub>13</sub>H<sub>14</sub>O<sub>4</sub> as 9-deoxygonioppyrone (**5**)<sup>3</sup> was given by

measurements of EIMS at  $m/z$  234 and HREIMS at 234.0890 (calcd 234.0892). The structure of **1** was established as 8-hydroxy-7-phenyl-2,6-dioxabicyclo[3.3.1]nonan-3-one, which was the same as that of **5**,

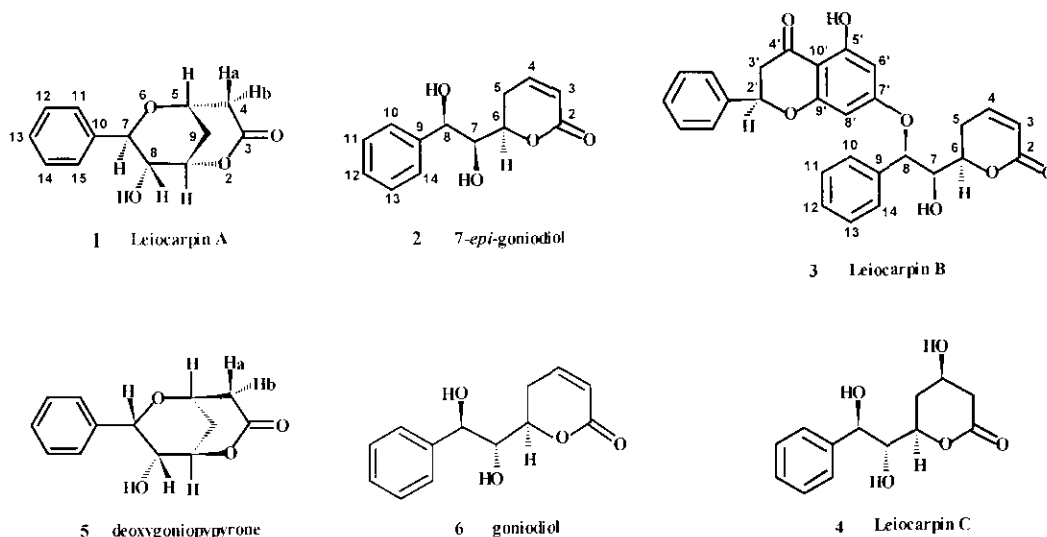


Figure 1 Structures of **1** - **6**

by analysis the  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, COLOC and MS spectra of **1**. Meanwhile, the spectra of  $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^{13}\text{C}$  COSY supported the above structure. However, the obvious distinction in  $[\alpha]_D$  values ( $-98^\circ$  for **1** and  $+12^\circ$  for **5**), and difference of  $J_{8/7}$  value and  $J_{8/9}$  value between **1** and **5** revealed that there was distinction in configuration between the two compounds. Finally, the relative configuration of **1** was determined as  $1S^*$ ,  $5S^*$ ,  $7R^*$  and  $8R^*$  (Figures 1 and 2) by analysis of both NOESY spectrum and the X-Ray crystallographic data,<sup>7</sup> while, those of **5** were  $1R^*$ ,  $5R^*$ ,  $7S^*$  and  $8R^*$  (Figure 1).

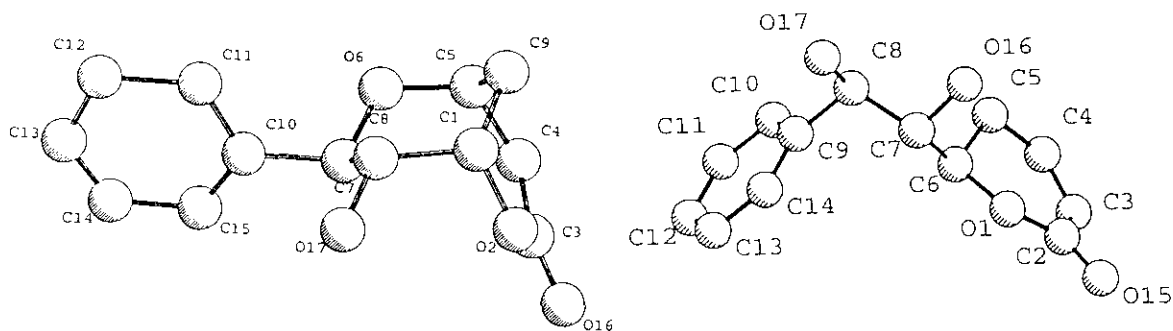


Figure 2 X-Ray Plot of **1** and **2**

Table 1. NMR Data of Compound (2) and (4)  
 (<sup>1</sup>H NMR 400 MHz and <sup>13</sup>C NMR 100 MHz, δ, ppm; J, Hz, in C<sub>5</sub>D<sub>5</sub>N<sub>2</sub>)

Compound Position	2		4	
	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, 9.8, 5.8, 2.6	146.55	4.79 m <sup>*</sup>	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, 4.8	78.62	4.39 dt, 7.5, 3.6	67.64
7	4.30 dd, 5.8, 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, 7.3	127.49	7.79 d, 7.6	127.95
11, 13	7.39 t, 7.3	128.62	7.35 t, 7.6	128.64
12	7.29 t, 7.3	127.57	7.25 t, 7.6	127.54

<sup>\*</sup> Only J=5.4 Hz could be measured in the <sup>1</sup>H NMR spectrum

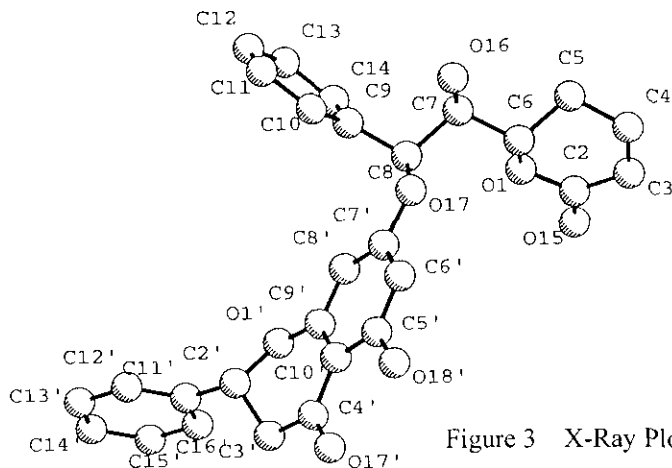
Compound (2), [ $\alpha$ ]<sub>D</sub><sup>20</sup> +85.4° (c 0.3, in MeOH), had the molecular weight suggested by a prominent peak at m/z 235 [MH]<sup>+</sup> in the FABMS spectrum. The presence of two hydroxyl groups was indicated by peaks at m/z 217 [MH-H<sub>2</sub>O]<sup>+</sup> and 199[MH-2H<sub>2</sub>O]<sup>+</sup> in the FABMS spectrum as well. The hydroxyl group at 3422 cm<sup>-1</sup> and  $\alpha$ ,  $\beta$ -unsaturated  $\delta$ -lactone band at 1704 cm<sup>-1</sup> were present in the IR spectrum. The same molecular formula C<sub>13</sub>H<sub>14</sub>O<sub>4</sub> and planar structure as a known styryllactone compound, goniodiol (6),<sup>4</sup> was given by the data of <sup>1</sup>H and <sup>13</sup>C NMR spectra of 2. Whereas the careful examination of the <sup>1</sup>H NMR gave distinguished differences of H-6, H-7 and H-8 either in chemical shifts or in coupling constants between 2 and goniodiol. The coupling constants of H-6/H-7 and H-7/H-8 in 2 were 5.8 and 3.7 Hz, while those in 6 were reported to be 2.2 and 7.0 Hz (6,7-*threo* and 7,8-*erythro*), respectively. This means that there were distinction of configuration in H-6, H-7 and H-8 between 2 and goniodiol. Finally, the relative configuration of 2 was established as 6,7-*erythro* and 7,8-*threo* or 6*R*\*, 7*S*\* and 8*R*\* by comparison of coupling constants and crystallographic analysis of X-ray,<sup>7</sup> and 2 was therefore determined as 7-*epi*-goniodiol (Figures 1 and 2).

Leiocarpin B (3) was colorless needle, mp 189-191°C, [ $\alpha$ ]<sub>D</sub><sup>24</sup> +28.8° (c 0.5 in CHCl<sub>3</sub>). The IR spectrum of 3 presented a hydroxyl band at 3500 cm<sup>-1</sup> and the carbonyl peak of a unsaturated  $\delta$ -lactone at 1700 cm<sup>-1</sup>. The <sup>13</sup>C NMR showed the existence of 28 carbons (Table 2), which were respectively attributed to two structural units: 7-*epi*-goniodiol (2) and pinocembrin (5,7-dihydroxydihydroflavone); two mono-substituted phenyls and the other 12 protons were also respectively corresponding to the above two structures in the <sup>1</sup>H and <sup>13</sup>C NMR. The molecular weight of 3 was indicated by a prominent peak at m/z

Table 2. NMR Spectral Data of Leiocrpin B (**3**)  
 ( $^1\text{H}$  NMR 400 MHz and  $^{13}\text{C}$  NMR 100 MHz,  $\delta$ , ppm; J, Hz, in  $\text{C}_5\text{D}_5\text{N}$ )

No.	H	C	No.	H	C
2	----	163.65	3'	3.12 dd, 17.1, 13.2; 2.78 dd, 17.1, 3.0	43.42
3	6.10 dd, 9.8, 1.8	121.17	4'	----	196.41
4	6.93 ddd, 9.8, 2.6, 1.8	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

472 in the EIMS spectrum, and the molecular formula  $\text{C}_{28}\text{H}_{24}\text{O}_7$  was determined by the peak at  $m/z$  472.1536 (calcd 472.1552) in the HREIMS. The structure of **3** was established as Figure 1 by the spectra of  $^1\text{H}$ - $^1\text{H}$  COSY, HECTOR and NOESY. 5'-Hydroxy-7'-*O*-dihydroflavone group positioned at C-8, that was suggested by the long-range coupling signal between H-8 and C-7' in the COLOC spectrum. The structure of **3** (Figure 3) was conformed by X-Ray crystallographic analysis.<sup>7</sup>



Compound (**2**) and (**3**) showed selective activities in test of trypan blue dye exclusion method. Under different concentration of 100, 10, 1, 0.1, 0.01  $\mu\text{g/mL}$ , the inhibition against HL-60 cells of compound (**2**) were 100, 100, 41, 21, 27%; and those of **3** were 100, 100, 55, 20, 4%.  $\text{IC}_{50}$  against Bel7404 (Hepatocarcinoma), Bcap32 (Breast Cancer), Hela of **2** were 0.96, 12.8, 3  $\mu\text{g/mL}$  respectively; while those of **3** were 0.79, >100, 30  $\mu\text{g/mL}$  against HL-60, K-562, U937 (Leukemia).

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

The relative configuration C-6, C-7 and C-8 of **4** could be determined by careful examination of coupling constants between H-6 and H-7, H-7 and H-8.<sup>4,5</sup> The coupling constants H-6/H-7 and H-7/H-8 in goniidiol (**6**) were reported to be 2.2 and 7.0 Hz (6,7-*threo*-7,8-*erythro*).<sup>4,6</sup> In compound (**4**), 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 **4** agreed with that of **6**, and was determined as 6,7-*threo* and 7,8-*erythro* (Figure 1).

In the NOE spectrum of **4**, the presence of correlation of Ph-H/H<sub>2</sub>-3, Ph-H/H<sub>2</sub>-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  $\alpha$ -orientation in the determined configuration (6,7-*threo*-7,8-*erythro*), H-4 was therefore assigned on  $\alpha$ -orientation. That was to say, the hydroxyl group at C-4 was identical as 4 $\beta$ -OH. Thus, the relative configuration of leiocarpin C (**4**) was determined as 6,7-*threo*-7,8-*erythro* and 4 $\beta$ -OH (Figure 1).

## EXPERIMENTAL

General Experimental Procedures -- Melting points were taken on a Koffler melting point apparatus and uncorrected. The UV spectra were obtained using a UV-210A Spectrophotometer. The IR spectra were measured on a Perkin-Elmer-577 Spectrophotometer. MS were performed on a Autospec-3000 Spectrometer and EIMS under 70ev. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 400 and 100 MHz, respectively, with a Bruker AM-400 Spectrometer. Elemental analyses were carried out on an EA-MOD1106 instrument. Silica gel-H (made in Qingdao Marine Chemical and Industrial Factory, China) was used for column chromatography and pre-coated Silica-G plates were employed for analytical TLC.

Plant Material -- The stem bark of *Goniiothalamus leiocarpus* used in this investigation was collected in south of Yunnan province, China. A voucher specimen of this plant was deposited in Kunming Institute of Botany, Kunming, China.

Extraction and Isolation -- The powdered the stem bark (5 kg) was extracted with EtOH (10 L  $\times$  3) for 72 h at rt. The alcohol was concentrated and then dried *in vacuo* to give 830 g of the dark brown resin. 200 g of EtOH extract was separated into three fractions by silica gel column (500 g) chromatography with  $\text{CHCl}_3$ , EtOAc and MeOH, repeatedly. The Fr. 1 (88 g) was carried out silica gel chromatography with gradient mixture of  $\text{CHCl}_3$  and MeOH, and gave the crude crystals of **2** (800 mg,  $\text{CHCl}_3$ -MeOH 99:1), **1** (3.2 g,  $\text{CHCl}_3$ -MeOH 98:2), **3** (1.2 g,  $\text{CHCl}_3$ -MeOH 95:5) and **4** (510 mg,  $\text{CHCl}_3$ -MeOH 90:10). These crude crystals were recrystallized in the different mixture of solvents to yield colorless needles of **1** (2 g,  $\text{Me}_2\text{CO}$ -Petrol), **2** (500 mg, EtOAc-Ben), **3** (800 mg,  $\text{CHCl}_3$ -MeOH) and **4** (470 mg, MeOH).

Bioassays -- Activity test were performed according to MTT method. Cancer cells with concentration of  $1.210^5$  cells/mL were inoculated into every cell of 96-well microculture. The cells were acted with different concentration of the compounds, and OD (optical density) values were taken on with microdalisa reder.

Leiocarpin A(**1**) mp 132-134 °C (  $\text{Me}_2\text{CO}$ -Petrol Ether );  $[\alpha]_D^{24}$  -98.42° (c 0.6,  $\text{CHCl}_3$ ); UV(MeOH) $\lambda_{\text{max}}$ : 207 (log  $\epsilon$  3.29) nm; IR (KBr) $\nu_{\text{max}}$  3360 ( hydroxyl ), 1720 (  $\delta$ -lactone ), 1660, 1180  $\text{cm}^{-1}$ ; EIMS m/z(%): 234(60)  $[\text{M}]^+$ , 216(7)  $[\text{M}-\text{H}_2\text{O}]^+$ , 188 (10), 177(17), 144(15), 128(35), 107(100), 91(40), 77(43), 69(80); HREIMS m/z 234.0890 for  $\text{C}_{13}\text{H}_{14}\text{O}_4$  (calcd 234.0892);  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data see References and Note. <sup>2</sup> Anal. Calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_4$ : C, 66.67; H, 5.98. Found: C, 67.00; H, 6.01.

7-*epi*-goniodiol (**2**) ( $\text{CHCl}_3$ -MeOH)  $[\alpha]_D^{23}$  +85.42° (c 0.6, MeOH); UV(MeOH) $\lambda_{\text{max}}$ : 206 (log  $\epsilon$  3.20); IR (KBr) $\nu_{\text{max}}$ : 3422, 2930, 1704, 1386, 1261, 1082, 1020  $\text{cm}^{-1}$ ; EIMS m/z(%): 216(33)  $[\text{M}-\text{H}_2\text{O}]^+$ , 200(13), 170(7), 155(13), 128(78), 110(50), 105(67), 91(100), 77(84); FABMS m/z: 235  $[\text{MH}]^+$ , 217  $[\text{MH}-\text{H}_2\text{O}]^+$ ;  $^1\text{H}$  and  $^{13}\text{C}$  NMR (in  $\text{C}_5\text{D}_5\text{N}$ ) see Table 1. Anal. Calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_4$ : C, 66.67; H, 5.98. Found: C, 66.84; H, 6.09.

Leiocarpin B (**3**) mp 189-191°C (EtOAc-Benzene);  $[\alpha]_D^{24}$  +28.79° (c 0.5,  $\text{CHCl}_3$ ); UV (MeOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ): 210(3.65), 289(3.33), 318(2.59) nm; IR(KBr) $\nu_{\text{max}}$ : 3500, 3040, 2910, 1700, 1620, 1560, 1240, 1160  $\text{cm}^{-1}$ ; EIMS m/z(%): 472(45)  $[\text{M}]^+$ , 345(48), 303(19), 256(78), 241(27), 179(66), 152(54), 131(60), 97(100), 69(94); HREIMS m/z 472.1536 for  $\text{C}_{28}\text{H}_{24}\text{O}_7$  (calcd 472.1552);  $^1\text{H}$  and  $^{13}\text{C}$  NMR (in  $\text{C}_5\text{D}_5\text{N}$ ) see Table 2. Anal. Calcd for  $\text{C}_{28}\text{H}_{24}\text{O}_7$ : C, 71.18; H, 5.08. Found: C, 71.07; H, 5.10.

Leiocarpin C (**4**) mp 131-132 °C (MeOH);  $[\alpha]_D^{24}$  -63.5° (c 0.5, MeOH); UV(MeOH) $\lambda_{\text{max}}$ : 207(log  $\epsilon$  2.90); IR (KBr) $\nu_{\text{max}}$ : 3400, 3200, 2920, 1710, 1690, 1485, 1440, 1200, 1100  $\text{cm}^{-1}$ ; EIMS m/z(%): 252(1)  $[\text{M}]^+$ , 234(60)  $[\text{M}-\text{H}_2\text{O}]^+$ , 216(10)  $[\text{M}-2\text{H}_2\text{O}]^+$ , 198(3)  $[\text{M}-3\text{H}_2\text{O}]^+$ , 188(5), 157(9), 128(47), 107(100), 91(80), 77(74), 60(90); HRFABMS m/z 253.0984 (calcd 253.1076) for  $\text{MH}^+$ ,  $^1\text{H}$  and  $^{13}\text{C}$  NMR see Table 1. Anal. Calcd for  $\text{C}_{13}\text{H}_{16}\text{O}_5$ : C, 61.90; H, 6.35. Found: C, 61.66; H, 6.37.

X-Ray Crystallographic Analysis of **1** Data collection -- A colorless rod of  $C_{13}H_{14}O_4$ , monoclinic. The intensity data collection were performed on a MAC DIP-2030K Probing Apparatus with  $MoK\alpha$  radiation and monochromator; the distance between the crystal and IP plate was 120mm( $d=120$ mm);  $\omega$  scan with 0-180°; oscillation angles  $\Delta\phi=3^\circ$ . The crystal data and data collection parameters were given in Table 3.

Table 3. Crystal Data and Data Collection Parameters of Compounds (**1**, **2** and **3**)

Data and parameters	<b>1</b>	<b>2</b>	<b>3</b>
Formula	$C_{13}H_{14}O_4$	$C_{13}H_{14}O_4$	$C_{28}H_{24}O_7$
Molecular weight	234	234	472
Space group	$P2_1$	$P1$	$P2_1$
a, Å	7.137(1)	8.668(1)	9.782(1)
b, Å	35.495(3)	8.686(1)	11.457(4)
c, Å	9.312(1)	9.576(1)	11.610(1)
$\alpha$ , °	---	109.20(1)	---
$\beta$ , °	91.14(1)	116.89(1)	114.80(8)
$\gamma$ , °	---	90.03(1)	---
V, Å <sup>3</sup>	2358.5(5)	597.6(1)	1183.11(49)
Z	2	2	2
$D_c$ , g·cm <sup>-3</sup>	1.314	1.302	1.329
Crystal dimensions, mm	0.4×0.5×0.6	---	0.4×0.7×0.3
2 $\theta$ rang, °	0-180	0-50	0-50
Data collected	3618	2092	2171
Unique data	3273	1844	1692
R <sub>f</sub>	0.133	0.043	0.041
R <sub>w</sub> ( $w=1/\sigma^2 F $ )	0.128	0.050	0.046
( $\Delta/\sigma$ )max	---	0.035	0.265
( $\Delta\rho$ )max e/Å <sup>3</sup>	---	0.260	0.250
( $\Delta\rho$ )min e/Å <sup>3</sup>	---	-0.210	-0.200

Structure solution and refinement -- The structure was solved using structure direct methods (SHELEXS-97). Initial carbon and oxygen atom coordinates were obtained from an E map. Using a series of difference Fourier syntheses and least-squares, 18 non-hydrogen atoms were located and their position were corrected, and the kind of atoms were determined. Hydrogen atoms except for which belonging hydroxyl groups were obtained in geometrical add-hydrogen method.  $R_f = 0.133$ ,  $R_w = 0.128$  ( $w=1/\sigma^2|F|$ ),  $GoF = 17.921$ . The crystal data and data collection parameters were given in Table 3.

X-Ray Crystallographic Analysis of **2**. Data Collection -- A colorless piece of  $C_{13}H_{14}O_4$ , triclinic. The intensity collection were performed using  $MoK\alpha$  radiation and graphite monochromator on a NoniousCAD-4 four-circle diffractometer, with the  $\omega$  scans,  $0^\circ < 2\theta < 50^\circ$ . 2092 reflection spots were collected and 1844 unique reflections were considered.

Structure Solution and Refinement -- The crystal structure was solved using direct method (SHELEXS-86). 34 non-hydrogen atoms were obtained from E map. Hydrogen atoms were obtained in succeeding difference Fourier syntheses and the structural parameters were refined in full-matrix least-squares,  $R_f = 0.043$ ,  $R_w = 0.050$  ( $w = 1/\sigma^2|F|$ ),  $(\Delta/\sigma)_{\max} = 0.035$ ,  $(\Delta\rho)_{\max} = 0.260 \text{ e}/\text{\AA}^3$ ,  $(\Delta\rho)_{\min} = -0.210 \text{ e}/\text{\AA}^3$ ,  $s = 1.052$ . The crystal data and data collection parameters were given in Table 3.

X-Ray Crystallographic Analysis of **3**. Procedures were essentially the same as those followed for the X-Ray crystallographic analysis of **2**, except the hydrogen positions and isotropic thermal parameters of **3** were refined, and the crystal data and collection were given in Table 3.

#### ACKNOWLEDGEMENTS

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#### REFERENCES AND NOTES

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2. NMR Data of Leiocarpin A (**1**).  $^1\text{H}$  NMR (400 MHz in  $\text{C}_5\text{D}_5\text{N}$ )  $\delta$ : 4.80 (br s, 1H, H-1), 2.81 (dd,  $J = 5.0$ , 19.5 Hz, 1H, H-4a), 2.90 (d,  $J = 19.5$  Hz, 1H, H-4b), 4.35 (br s, H-5), 4.41 (d,  $J = 8.8$  Hz, 1H, H-7), 3.45 (d,  $J = 8.8$  Hz, 1H, H-8), 2.11 (br s, 2H, H<sub>2</sub>-9), 7.25 - 7.43 (m, 5H, Ph);  $^{13}\text{C}$  NMR data of **1**  $\delta$  (ppm, in  $\text{CDCl}_3$ , 100 MHz): 76.88 (C-1), 169.21 (C-3), 36.35 (C-4), 65.62 (C-5), 73.92 (C-7), 72.27 (C-8), 29.58 (C-9), 138.21 (C-10), 127.41 (C-11, 15), 128.27 (C-12,14), 128.27 (C-13).
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