RIVULOBIRINS C AND D, TWO NOVEL NEW SPIROBICOUMARINS, FROM THE UNDERGROUND PART OF *PLEUROSPERMUM RIVULORUM*

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Two new spirobicoumarins, rivulobirins C and D (**1** and **2**), were isolated from the underground part of *Pleurospermum rivulorum*. They are characterized as two stereoisomers having a different configuration at the C-2 position resulting from the condensation of two heraclenol units, respectively, on the basis of spectral analysis.

KEY WORDS *Pleurospermum rivulorum*; Umbelliferae; spirobicoumarin; rivulobirins C and D

The underground part of *Pleurospermum rivulorum*, "Yunnan Qiang Huo," is a Chinese folk medicine used as an antipyretic, analgesic, and diaphoretic agent in local areas of Yunnan province, China. In the course of our studies on the phenolic components of umbelliferous plants, we investigated the constituents of this medicinal plant, and isolated two new bicoumarins, rivulobirins A and B, together with 11 known coumarins.[1] The continuing search led us to isolate two new spirobicoumarins, rivulobirins C and D (**1** and **2**). This communication deals with the structural elucidation of **1** and **2**.

The ethyl acetate extract of the underground part of *P. rivulorum* was subjected to a combination of column chromatography over silica gel and preparative TLC to yield **1** and **2**.

Rivulobirin C (**1**), a colorless viscous oil, $[\alpha]_D$ +65.4°, was assigned the molecular formula $C_{32}H_{30}O_{11}$ ($[M]^+$ *m/z* 590.1778) by HR-EI-MS. The ^{1}H-NMR spectrum exhibited the presence of two heraclenol (**3**) units. However, the ^{13}C-NMR spectrum of **1** showed one carbonyl carbon signal attributable to a lactone carbon and one signal assigned to a carbon linked to three oxygen atoms at 118.3 ppm, indicating that one of two lactone moieties was replaced by the spiro form in **1**. The gross structure of **1** was determined by extensive 2D-NMR experiments including studies of ^{1}H-^{1}H COSY, HMQC, and HMBC (Fig. 1) spectra. The absolute stereostructure of **1** was determined based on the analysis of its NOESY spectrum (Fig. 2) and the formation of its derivatives, heraclenol, isogosferol, and pabularinone with acid treatment.

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Table. NMR Data for Compounds **1** - **3** in $CDCl_3$

	^1H			^{13}C			^1H		^{13}C	
	1	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**1**	**2**
2				118.3	117.4	160.1	2'		160.4	160.2
3	5.76 d (9.7)	5.72 d (9.6)	6.37 d (9.6)	119.5	119.2	114.7	3' 6.36 d (9.6)	6.34 d (9.6)	114.7	114.7
4	6.83 d (9.7)	6.85 d (9.6)	7.76 d (9.6)	129.1	129.7	144.3	4' 7.73 d (9.6)	7.73 d (9.6)	144.3	144.2
4a				116.9	117.0	116.4	4'a		116.4	116.4
5	7.08 s	7.09 s	7.39 s	113.2	113.3	113.7	5' 7.32 s	7.35 s	113.7	113.7
6				122.8	122.8	126.0	6'		125.9	126.0
7				147.3	147.5	147.9	7'		148.0	147.8
8				131.5[a]	131.8	131.5	8'		131.6[a]	131.2
8a				141.3	141.3	143.2	8'a		143.3	143.2
9	7.55 d (2.1)	7.55 d (2.2)	7.70 d (2.3)	144.9	145.0	146.8	9' 7.66 d (2.2)	7.65 d (2.2)	146.8	146.7
10	6.69 d (2.1)	6.69 d (2.2)	6.83 d (2.3)	106.8	106.8[b]	106.8	10' 6.77 d (2.2)	6.79 d (2.2)	106.6	106.7[b]
11	4.48 dd (10.3, 2.7)	4.62 dd (10.3, 3.0)	4.75 dd (10.2, 2.7)	74.9	75.3	75.7	11' 4.86 dd (10.3, 6.6)	4.76 dd (10.3, 6.2)	72.8	71.2
	4.18 dd (10.3, 8.2)	4.33 dd (10.3, 7.6)	4.42 dd (10.2, 7.9)				4.83 dd (10.3, 6.6)	4.52 dd (10.3, 6.2)		
12	3.68 ddd (8.2, 3.9, 2.7)	3.78 ddd (7.6, 4.4, 3.0)	3.89 ddd (7.9, 4.1, 2.7)	75.9	75.8	76.0	12' 4.55 t (6.6)	4.92 t (6.2)	83.1	80.8
13				71.2	71.6	71.5	13'		83.0	83.3
14	1.17 s	1.29 s	1.31 s	24.8	25.3	25.0	14' 1.59 s	1.44 s	28.3	22.5
15	1.20 s	1.31 s	1.34 s	26.5	26.5	26.6	15' 1.76 s	1.76 s	22.7	27.1
12-OH	3.42 d (3.9)	3.56 d (4.4)	3.54 d (4.1)							
13-OH	2.65 s	2.91 s	2.74 s							

Chemical shifts are in δ values and followed by multiplicities and *J* values (in Hz). a, b) Assignment may be reversed.

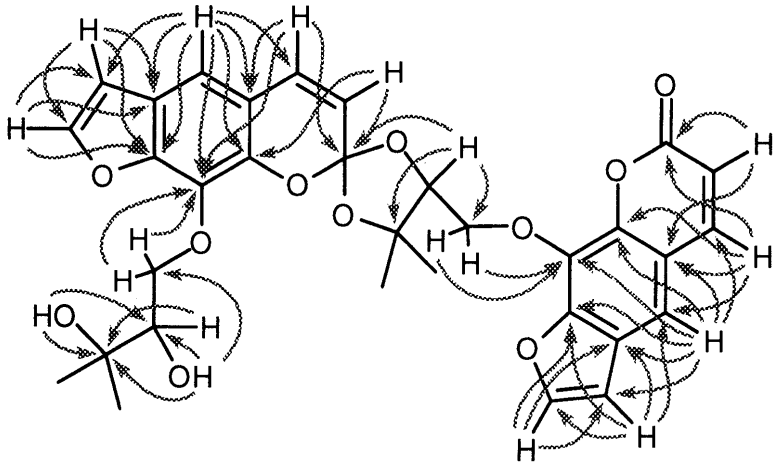

Fig. 1 HMBC Correlations of **1**

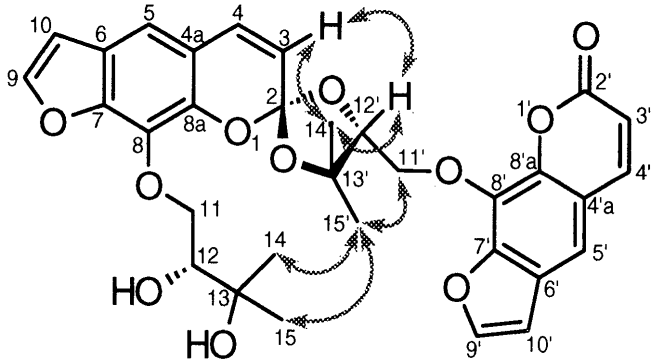

Fig.2 NOE Correlations of **1**

Rivulobirin D (**2**), a colorless viscous oil, $[\alpha]_D$ -19.8°, was assumed to be a stereoisomer of **1** from the analysis of the HR-EI-MS ([M]$^+$ *m/z* 590.1781). Comparison of ^{1}H and ^{13}C-NMR spectral data including ^{1}H-^{1}H COSY, HMQC, and HMBC experiments suggested that **2** differed from **1** only in the configuration at the C-2 position. This presumption was proved by analysis of the NOESY spectrum (Fig. 3) of **2**. Thus, the structures of **1** and **2** were established.

Rivulobirins C and D are the first examples of spirobicoumarin.

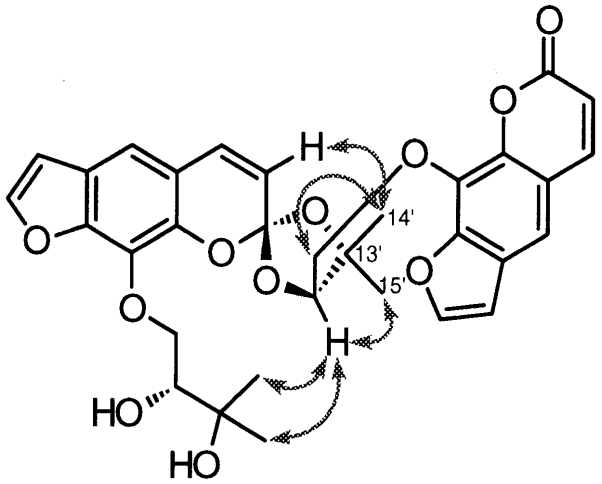

Fig.3 NOE Correlations of **2**

REFERENCE

1)Xiao Y.-Q., Liu X.-H., Taniguchi M. and Baba K., *Phytochemistry*, **45**, 1275-1277 (1997).

(Received April 20, 1998; accepted May 18, 1998)