

Rivulotrins A and B from *Pleurospermum rivulorum*

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Two new spirotrifuranocoumarins, rivulotrins A and B (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 and one isogosferol units, respectively, on the basis of spectral analysis.

Key words *Pleurospermum rivulorum*; Umbelliferae; spirotrifuranocoumarin; rivulotrins A and B

During of the course of studies on the phenolic components of umbelliferous plants, we reported new bicoumarins, rivulobirins A—D, along with 11 known coumarins from the underground part of *Pleurospermum rivulorum*.^{1,2)} Continued investigation on the coumarin fraction by repeated chromatography on silica gel resulted in the isolation of two novel spirotrifuranocoumarins, rivulotrins A and B (1 and 2). This communication deals with the structure elucidation of 1 and 2.

Rivulotrins A (1), a colorless viscous oil, was assigned the molecular formula C₄₈H₄₂O₁₅ ([M]⁺ *m/z* 858.2510) by HR-EI-MS. The ¹H-NMR spectrum showed the presence of three C-8-substituted linear-type furanocoumarin fragments, a 3-methyl-3-butenyl-1,2-dioxy group and two pairs of the 3-methylbutyl-1,2,3-trioxy group. Thus 1 was assumed to be a structure resulting from the condensation of two heraclenol and one isogosferol units. These functional groups were also identified by ¹³C-NMR spectroscopy. However, the absence

Table 1. ¹H-NMR Data for Rivulotrins A (1) and B (2) in CDCl₃

H	1	2	H	1	2	H	1	2
3	5.70 d (9.6)	5.73 d (9.7)	3'	6.29 d (9.6)	6.30 d (9.6)	3''	6.33 d (9.6)	6.34 d (9.5)
4	6.82 d (9.6)	6.80 d (9.7)	4'	7.66 d (9.6)	7.67 d (9.6)	4''	7.72 d (9.6)	7.71 d (9.5)
5	7.03 s	7.01 s	5'	7.20 s	7.20 s	5''	7.34 s	7.30 s
9	7.49 d (2.2)	7.47 d (2.3)	9'	7.61 d (2.2)	7.57 d (2.3)	9''	7.63 d (2.2)	7.65 d (2.3)
10	6.64 d (2.2)	6.63 d (2.3)	10'	6.67 d (2.2)	6.66 d (2.3)	10''	6.77 d (2.2)	6.74 d (2.3)
11	4.48 dd (10.3, 3.2)	4.08 dd (10.1, 8.5)	11'	4.39 dd (10.3, 6.8)	4.33 dd (10.2, 5.0)	11''	4.73 dd (10.3, 5.8)	4.82 dd (10.3, 6.9)
	4.21 dd (10.3, 8.1)	4.37 dd (10.1, 3.0)		4.37 dd (10.3, 5.0)	4.35 dd (10.2, 6.6)		4.50 dd (10.3, 6.8)	4.86 dd (10.3, 6.4)
12	3.88 ddd (8.1, 3.4, 3.2)	3.74 br dd (8.5, 3.0)	12'	4.55 dd (6.8, 5.0)	4.48 dd (6.6, 5.0)	12''	4.82 dd (6.8, 5.8)	4.50 dd (6.9, 6.4)
14	1.33 s	1.22 s	14'	5.13 br s	4.91 br s	14''	1.43 s	1.56 s
				4.94 br s	5.08 br s			
15	1.26 s	1.16 s	15'	1.82 s	1.78 s	15''	1.75 s	1.73 s
12-OH	3.30 d (3.4)	3.07 br s						

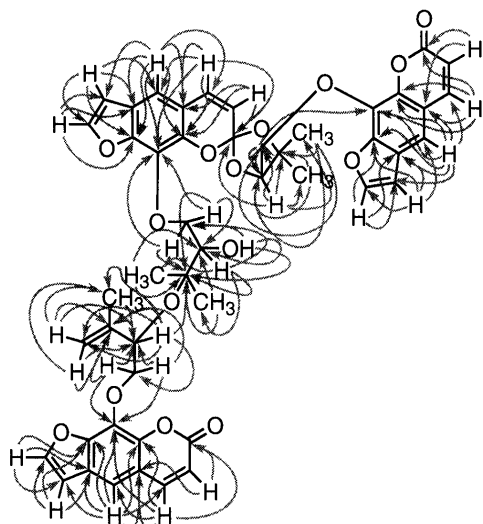
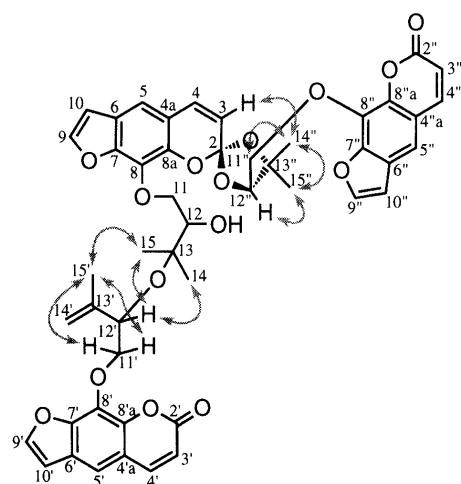
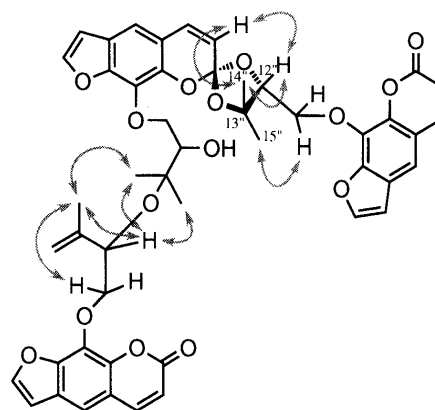
Chemical shifts are in δ values and followed by multiplicities and *J* values (in Hz).

Table 2. ¹³C-NMR Data for Rivulotrins A (1) and B (2) in CDCl₃

C	1	2	C	1	2	C	1	2
2	117.35	118.23	2'	160.30	160.37 ^{e)}	2''	160.04	160.33 ^{e)}
3	119.07	119.35	3'	114.47	114.61	3''	114.69	114.71
4	129.75	129.21	4'	144.21	144.24 ^{f)}	4''	144.14	144.21 ^{f)}
4a	116.96	116.93	4'a	116.28	116.37 ^{g)}	4'a	116.38	116.41 ^{g)}
5	112.84	112.70	5'	112.84	112.87	5''	113.69	113.51
6	122.69	122.77	6'	125.90 ^{c)}	125.96	6''	125.95 ^{c)}	126.05
7	147.70 ^{a)}	147.52 ^{d)}	7'	147.56	147.60 ^{d)}	7''	147.77 ^{a)}	147.91
8	132.24	132.17	8'	132.00	132.08	8''	131.16	131.53
8a	141.49	141.42	8'a	142.94	143.00	8'a	143.10	143.26
9	144.81	144.72	9'	146.57	146.58	9''	146.77	146.88
10	106.58 ^{b)}	106.72	10'	106.52 ^{b)}	106.57 ^{h)}	10''	106.64 ^{b)}	106.66 ^{h)}
11	74.72	74.54	11'	75.67	75.70	11''	71.14	72.72
12	76.37	76.45	12'	74.93	74.99	12''	80.63	83.09
13	78.05	78.01	13'	144.81	144.81	13''	83.18	82.89
14	22.02	21.98	14'	113.42	113.49	14''	22.53	28.35
15	22.32	22.29	15'	18.61	18.65	15''	27.44	22.68

Chemical shifts are in δ values. a—h) Assignments may be reversed.

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Fig. 1. HMBC Correlations of **1**Fig. 2. NOE Correlations of **1**Fig. 3. NOE Correlations of **2**

of one of three lactone carbonyl signals arising from the coumarin ring was observed, similar to those of rivulobirins C and D, indicating that one lactone moiety was also replaced by the spiro form in **1**. The entire structure of **1** was determined by extensive 2D-NMR experiments including studies of ^1H - ^1H COSY, HMQC, and HMBC (Fig. 1) spectra. The relative configurations of the C-2 and C-12'' positions in **1** were confirmed by the analysis of its NOESY spectrum (Fig. 2) and comparison of the spectral data of **1** with those of ribulobirin A, C, and D.^{1,2)}

Rivulotririn B (**2**), a colorless viscous oil, was assumed to be a stereoisomer of **1** from the analysis of the HR-EI-MS ($[\text{M}]^+$ m/z 858.2510). Comparison of NMR spectral data including ^1H - ^1H COSY, HMQC, HMBC, and NOESY (Fig. 3) experiments suggested that **2** differed from **1** in the configuration at the C-2 (spiro form) or at the C-12'' position. Thus the structures of **1** and **2** were established as shown.

Rivulotririns A and B (**1** and **2**) are the first examples of trifuranocoumarin including the spiro ring.

References

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