SUPPLEMENTARY MATERIAL

Two benzaldehyde derivatives and their artifacts from a gorgonian-derived *Eurotium* sp. fungus

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Abstract:

Two new benzaldehyde derivatives, named 3'-OH-tetrahydroauroglaucin (**1**) and (3'*S**, 4'*R**)-6-(3',5-epoxy-4'-hydroxy-1'-heptenyl)-2-hydroxy-3-(3''-methyl-2''-butenyl)benzaldehyde (**2**), were isolated from a gorgonian-derived *Eurotium* sp. fungus. Their structures were determined by extensive spectroscopic analysis including NMR and MS spectra. Dissolved **1** in CDCl₃ for several days could be detected its 2*H*-chromene skeleton derivatives (**1a/1b**), a pair of enantiomers with opposite configurations at C-3'. Compound **2** was also found to chemically convert to a pair of epimers non-enzymatically. The plausible mechanism to form the 2*H*-chromene artifacts with racemization at C-3' undergoing nucleophilic substitution (S_N1) was proposed.

Keywords: gorgonian-derived fungus; *Eurotium* sp.; benzaldehyde derivative; 2*H*-chromene; racemization

List of Supplementary Material

Table S1. ^1H and ^{13}C NMR Spectroscopic Data for **1** and **2** at 600 (^1H) and 150 (^{13}C) MHz

Figure S1. Selected ^1H , ^1H -COSY (bold line) and HMBC (arrow) correlations of **1**

Figure S2. ^1H NMR (600 MHz, CDCl_3) spectrum of compound **1**

Figure S3. Partial ^1H NMR (600 MHz, CDCl_3) spectrum of compound **1**

Figure S4. ^{13}C NMR (150 MHz, CDCl_3) spectrum of compound **1**

Figure S5. HMQC (CDCl_3) spectrum of compound **1**

Figure S6. ^1H - ^1H COSY (CDCl_3) spectrum of compound **1**

Figure S7. HMBC (CDCl_3) spectrum of compound **1**

Figure S8. HRESIMS spectrum of compound **1**

Figure S9. ^1H NMR (600 MHz, CDCl_3) spectrum of compounds **1a/1b**

Figure S10. Partial ^1H NMR (600 MHz, CDCl_3) spectrum of compounds **1a/1b**

Figure S11. HRESIMS spectrum of compounds **1a/1b**

Figure S12. ^1H NMR (600 MHz, CDCl_3) spectrum of compound **2**

Figure S13. Partial ^1H NMR (600 MHz, CDCl_3) spectrum of compound **2**

Figure S14. ^{13}C NMR (150 MHz, CDCl_3) spectrum of compound **2**

Figure S15. ^1H NMR (600 MHz, CDCl_3) spectrum of compounds **2/2a**

Figure S16. HRESIMS spectrum of compounds **2/2a**.

Table S1. ^1H and ^{13}C NMR Spectroscopic Data for **1** and **2** at 600 (^1H) and 150 (^{13}C) MHz

position	1		2	
	δ_{C} , type	δ_{H} , mult. (J in Hz)	δ_{C} , type	δ_{H} , mult. (J in Hz)
1	105.3, C		106.5, C	
2	154.4, C		159.2, C	
3	129.9, C		138.3, C	
4	124.6, CH	7.01, s	124.9, CH	6.95, s
5	144.9, C		146.8, C	
6	122.4, C		119.7, C	
7	195.1, CH	10.08, s	192.9, CH	10.29, s
1'	117.0, CH	6.76, d (16.2)	118.9, CH	7.06, dd (10.2, 1.8)
2'	128.2, CH	5.99, dd (16.2, 5.4)	123.8, CH	5.96, dd (10.2, 3.0)
3'	71.7, CH	4.39, dd (6.0, 5.4)	77.3, CH	4.73, dd (3.6, 3.0)
4'	26.8, CH ₂	1.66, m	72.3, CH	3.93, ddd (7.8, 4.2, 3.6)
5'	36.3, CH ₂	1.38, m	33.3, CH ₂	1.59, m
6'	21.7, CH ₂	1.38, m	18.3, CH ₂	1.41, m
7'	13.2, CH ₃	0.93, t (6.6)	13.3, CH ₃	0.97, t (6.6)
1''	26.4, CH ₂	3.32, d (7.2)	26.6, CH ₂	3.30, d (7.2)
2''	120.6, CH	5.28, brt (7.2)	120.1, CH	5.27, brt (7.2)
3''	133.2, C		134.8, C	
4''	25.0, CH ₃	1.75, s	25.1, CH ₃	1.76, s
5''	16.9, CH ₃	1.69, s	17.1, CH ₃	1.69, s
2-OH		11.76, s		11.77, s
5-OH		5.55, brs

Figure S2. ^1H NMR (600 MHz, CDCl_3) spectrum of compound **1**

Figure S3. Partial ^1H NMR (600 MHz, CDCl_3) spectrum of compound **1**

Figure S4. ^{13}C NMR (150 MHz, CDCl_3) spectrum of compound **1**

Figure S5. HMQC (CDCl_3) spectrum of compound **1**

Figure S6. ^1H - ^1H COSY (CDCl_3) spectrum of compound **1**

Figure S7. HMBC (CDCl_3) spectrum of compound **1**

20121108-E633A_121108104725 #174-183 RT: 1.63-1.71 AV: 10 NL: 2.77E5
T: FTMS - p ESI sid=50.00 Full ms [70.00-2000.00]

Figure S8. HRESIMS spectrum of compound 1

Figure S9. ¹H NMR (600 MHz, CDCl₃) spectrum of compounds 1a/1b

Figure S10. Partial ^1H NMR (600 MHz, CDCl_3) spectrum of compounds **1a/1b**

Figure S11. HRESIMS spectrum of compounds **1a/1b**

Figure S12. ^1H NMR (600 MHz, CDCl_3) spectrum of compound **2**

Figure S13. Partial ^1H NMR (600 MHz, CDCl_3) spectrum of compound **2**

Figure S14. ¹³C NMR (150 MHz, CDCl₃) spectrum of compound **2**

Figure S15. ¹H NMR (600 MHz, CDCl₃) spectrum of compounds **2/2a**

20121105-E663_121102095601 #109-111 RT: 1.00-1.02 AV: 3 NL: 1.79E6
T: FTMS - p ESI Full ms [150.00-2000.00]

Figure S16. HRESIMS spectrum of compounds **2/2a**