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-tetrahydroaurolaucin (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 2H-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 2H-chromene artifacts with racemization at C-3’ undergoing nucleophilic substitution (SN1) was proposed.

Keywords: gorgonian-derived fungus; Eurotium sp.; benzaldehyde derivative; 2H-chromene; racemization
Table S1. $^1$H and $^{13}$C NMR Spectroscopic Data for 1 and 2 at 600 ($^1$H) and 150 ($^{13}$C) MHz

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

Figure S2. $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compound 1

Figure S3. Partial $^1$H 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. $^1$H–$^1$H 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. $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compounds 1a/1b

Figure S10. Partial $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compounds 1a/1b

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

Figure S12. $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compound 2

Figure S13. Partial $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compound 2

Figure S14. $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of compound 2

Figure S15. $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compounds 2/2a

Figure S16. HRESIMS spectrum of compounds 2/2a.
Table S1. $^1$H and $^{13}$C NMR Spectroscopic Data for 1 and 2 at 600 ($^1$H) and 150 ($^{13}$C) MHz

| position | $\delta_c$, type | $\delta_H$, mult. ($J$ in Hz) | $\delta_c$, type | $\delta_H$, 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        |                               |                  |                               |
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Figure S9. $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compounds 1a/1b
Figure S10. Partial $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compounds 1a/1b

Figure S11. HRESIMS spectrum of compounds 1a/1b
Figure S12. $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compound 2

Figure S13. Partial $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compound 2
Figure S14. $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of compound 2

Figure S15. $^1$H NMR (600 MHz, CDCl$_3$) spectrum of compounds 2/2a
Figure S16. HRESIMS spectrum of compounds 2/2a