Supplementary material

Two new tricycloalternarene esters from an alga-epiphytic isolate of *Alternaria alternata*

Zhen-Zhen Shi<sup>ab</sup>, Sheng-Tao Fang<sup>a</sup>, Feng-Ping Miao<sup>a</sup> and Nai-Yun Ji<sup>a</sup>*

<sup>a</sup>Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China;
<sup>b</sup>University of Chinese Academy of Sciences, Beijing 100049, China

**Abstract**

Two new tricycloalternarene-type meroterpenes, 17-<i>O</i>-methyltricycloalternarene D (1) and methyl nortricycloalternarene (4), and two known congeners, TCA D (2) and TCA 1b (3), were isolated from the culture of a marine red alga-epiphytic fungal strain (k21-1) of *Alternaria alternata*. The planar structures and relative configurations of these two new compounds were unequivocally identified by a combination of 1D/2D NMR, UV, IR, and mass spectra and by comparison with literature data, and the absolute configurations were assigned by analysis of ECD spectra. Compounds 1-4 were evaluated for growth inhibition of four marine plankton species, but they appeared weak or moderate to inhibit them.

**Keywords:** tricycloalternarene; meroterpene; *Alternaria alternata*
Contents

S3: **Table S1.** $^1$H and $^{13}$C NMR data for 1 and 4 (in CDCl$_3$);
S4: **Table S2.** Inhibitory or toxic effects on four marine plankton of 1-4 at 100 μg/mL;
S5: **Figure S1.** Key HMBC & $^1$H-$^1$H COSY correlations of 1 and 4;
S6: **Figure S2.** Key NOESY correlations of 1 and 4;
S7: **Figure S3.** Experimental ECD spectra of 1 and 4;
S8: **Figure S4.** $^1$H NMR spectrum of 1;
S9: **Figure S5.** $^{13}$C NMR and DEPT spectra of 1;
S10: **Figure S6.** HSQC spectrum of 1;
S11: **Figure S7.** HMBC spectrum of 1;
S12: **Figure S8.** $^1$H-$^1$H COSY spectrum of 1;
S13: **Figure S9.** NOESY spectrum of 1;
S14: **Figure S10.** EIMS spectrum of 1;
S15: **Figure S11.** HREIMS spectrum of 1;
S16: **Figure S12.** IR spectrum of 1;
S17: **Figure S13.** UV spectrum of 1;
S18: **Figure S14.** $^1$H NMR spectrum of 4;
S19: **Figure S15.** $^{13}$C NMR and DEPT spectra of 4;
S20: **Figure S16.** HSQC spectrum of 4;
S21: **Figure S17.** HMBC spectrum of 4;
S22: **Figure S18.** $^1$H-$^1$H COSY spectrum of 4;
S23: **Figure S19.** NOESY spectrum of 4;
S24: **Figure S20.** EIMS spectrum of 4;
S25: **Figure S21.** HREIMS spectrum of 4;
S26: **Figure S22.** IR spectrum of 4;
S27: **Figure S23.** UV spectrum of 4.
| pos | $\delta_H$ (mult., J in Hz) | $\delta_C$ | $\delta_H$ (mult., J in Hz) | $\delta_C$ |
|-----|-----------------|-----|-----------------|-----|
| 1a  | 3.91 (dd, 10.7, 5.9) | 69.6 (CH$_2$) | | |
| 1b  | 3.82 (dd, 10.7, 6.9) | | | |
| 2   | 1.73 (m) | 32.6 (CH) | | |
| 3a  | 1.31 (m) | 33.7 (CH$_2$) | | |
| 3b  | 1.07 (m) | | | |
| 4a  | 1.25 (m) | 24.8 (CH$_2$) | 2.18 (m) | 32.3 (CH$_2$) |
| 4b  | 1.16 (m) | | | |
| 5a  | 1.43 (m) | 35.0 (CH$_2$) | 1.77 (m) | 29.8 (CH$_2$) |
| 5b  | 1.23 (m) | 1.62 (m) | | |
| 6   | 1.97 (m) | 33.0 (CH) | 1.94 (m) | 32.2 (CH) |
| 7   | 150.6 (C) | 149.3 (C) | | |
| 8   | 5.28 (br s) | 119.8 (CH) | 5.35 (br s) | 120.6 (CH) |
| 9a  | 2.56 (br d, 16.1) | 45.1 (CH$_2$) | 2.61 (br d, 16.3) | 45.1 (CH$_2$) |
| 9b  | 2.40 (br d, 16.1) | 2.46 (br d, 16.3) | | |
| 10  | 88.1 (C) | | 88.9 (C) | |
| 11  | 2.72 (m) | 46.7 (CH) | 2.79 (m) | 46.8 (CH) |
| 12a | 2.61 (br d, 17.0) | 15.6 (CH$_2$) | 2.61 (br d, 16.7) | 15.2 (CH$_2$) |
| 12b | 2.20 (br dd, 16.8, 6.5) | | 2.22 (overlap) | |
| 13  | 106.7 (C) | | 107.7 (C) | |
| 14  | 171.2 (C) | | 170.1 (C) | |
| 15a | 2.48 (dt, 17.6, 5.3) | 27.1 (CH$_2$) | 4.36 (br dd, 8.3, 5.0) | 66.6 (CH) |
| 15b | 2.33 (m) | | | |
| 16a | 2.15 (dq, 12.9, 5.1) | 27.3 (CH$_2$) | 2.24 (m) | 29.1 (CH$_2$) |
| 16b | 1.91 (dtd, 12.9, 9.4, 5.2) | 1.92 (m) | | |
| 17a | 3.64 (dd, 9.8, 4.3) | 79.7 (CH) | 2.57 (ddd, 16.7, 5.9, 4.7) | 33.7 (CH$_2$) |
| 17b | | | 2.31 (dd, 16.9, 10.7, 4.8) | | |
| 18  | | | 195.8 (C) | 196.9 (C) |
| 2'  | 0.89 (d, 6.7) | 17.0 (CH$_3$) | | |
| 6'  | 0.93 (d, 6.9) | 20.2 (CH$_3$) | 0.96 (d, 6.9) | 20.3 (CH$_3$) |
| 10' | 1.42 (s) | 23.8 (CH$_3$) | 1.49 (s) | 23.7 (CH$_3$) |
| CH$_3$O | 3.50 (s) | 58.3 (CH$_3$) | 3.63 (s) | 51.7 (CH$_3$) |
| CH$_2$CO | 2.05 (s) | 21.1 (CH$_3$) | | |
| CH$_3$CO | 171.5 (C) | | | |
Table S2. Inhibitory or toxic effects on four marine plankton of 1-4 at 100 μg/mL.

|     | *Heterosigma akashiwo*/% | *Chattonella marina*/% | *Prorocentrum donghaiense*/% | *Artemia salina*/% |
|-----|--------------------------|------------------------|------------------------------|-------------------|
| 1   | 39.4 ± 0.5               | 59.3 ± 1.8             | 45.2 ± 1.1                   | 27.3 ± 2.0        |
| 2   | 18.9 ± 1.2               | 78.5 ± 0.7             | 33.2 ± 2.9                   | 12.6 ± 1.6        |
| 3   | 43.0 ± 0.3               | 61.6 ± 0.9             | 43.9 ± 1.3                   | 73.0 ± 4.0        |
| 4   | 9.6 ± 0.9                | 28.9 ± 1.8             | 18.9 ± 1.0                   | 45.8 ± 2.6        |
| K₂Cr₂O₇ | 100.0                  | 100.0                  | 100.0                        | 100.0             |
Figure S1. Key HMBC & $^1$H-$^1$H COSY correlations of 1 and 4.
Figure S2. Key NOESY correlations of 1 and 4.
Figure S3. Experimental ECD spectra of 1 and 4;
Figure S4. $^1$H NMR spectrum of 1.
Figure S5. $^{13}$C NMR and DEPT spectra of 1.
Figure S6. HSQC spectrum of 1.
Figure S7. HMBC spectrum of 1.
Figure S8. $^1$H-$^1$H COSY spectrum of 1.
Figure S9. NOESY spectrum of 1.
Figure S10. EIMS spectrum of 1.
Figure S11. HREIMS spectrum of 1.
Figure S12. IR spectrum of 1.
Figure S13. UV spectrum of 1.
Figure S14. $^1$H NMR spectrum of 4.
Figure S15. $^{13}$C NMR and DEPT spectra of 4.
Figure S16. HSQC spectrum of 4.
Figure S17. HMBC spectrum of 4.
Figure S18. $^1\text{H}-${$^1\text{H}$} COSY spectrum of 4.
Figure S19. NOESY spectrum of 4.
Figure S20. EIMS spectrum of 4.
Figure S21. HREIMS spectrum of 4.
Figure S22. IR spectrum of 4.
Figure S23. UV spectrum of 4.