Electronic Supplementary Information

Ancistrocyclinones A and B, unprecedented pentacyclic N,C-coupled naphthylisoquinoline alkaloids, from the Chinese liana Ancistrocladus tectorius

Raina Seupel\textsuperscript{a}, Yasmin Hemberger\textsuperscript{a}, Doris Feineis,\textsuperscript{a}

Minjuan Xu\textsuperscript{b,c}, Ean-Jeong Seo\textsuperscript{d}, Thomas Efferth\textsuperscript{d},

Gerhard Bringmann\textsuperscript{a,*},

\textsuperscript{a}Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany

\textsuperscript{b}Key Laboratory of Systems Biomedicine, Shanghai Center for Systems Biomedicine, Shanghai Jia Tong University, 800 Dongchuan Road, Shanghai 200240, P.R. China

\textsuperscript{c}Marine Drugs Research Center, College of Pharmacy, Jinan University, 601 Huangpu Avenue West, Guangzhou 510632, P.R. China

\textsuperscript{d}Institute of Pharmacy and Biochemistry, Department of Pharmaceutical Biology, University of Mainz, Staudinger Weg 5, D-55128 Mainz, Germany
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- Figure 39: Cytotoxic activities of ancistrocladinium A (7a/b) and ancistrocyclinone A (5)
Table 1: $^1$H and $^{13}$C NMR data of ancistrocyclinone A (5) and B (6) in MeOD (400 MHz and 150 MHz).\(^a\)

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<th>Position</th>
<th>$\delta_\text{H}$</th>
<th>$\delta_\text{C}$</th>
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<th>$\delta_\text{C}$</th>
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<td>148.8</td>
<td>148.6</td>
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<td>3.13 (dd, 16.7, 1.7)</td>
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<td>3.51 (dd, 15.6, 5.1)</td>
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<td>139.4</td>
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<td>1'</td>
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<td>6.90 (d, 1.4)</td>
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<td>163.7</td>
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<td>4.25 (s)</td>
<td>57.9</td>
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\(^a\) Multiplicities and coupling constants $J$ (Hz) are shown in parentheses, $\delta$ values are given in ppm.
Figure 1: $^1$H NMR spectrum of ancistrocyclinone A (5) in MeOD.
Figure 2: $^{13}$C NMR spectrum of ancistrocyclinone A (5) in MeOD.
Figure 3: DEPT NMR spectrum of ancistrocyclinone A (5) in MeOD.
Figure 4: $^1$H,$^1$H-COSY spectrum of ancistrocyclinone A (5) in MeOD.
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Figure 7: HMBC spectrum of ancistrocyclinone A (5) in MeOD.
Figure 8: HRESI mass spectrum of ancistrocyclinone A (5).
Figure 9: IR spectrum of ancistrocyclone A (5).
**Figure 10:** ECD spectrum of ancistrocyclinone A (5).
Figure 11: Oxidative degradation products of ancistrocyclinone A (5).

Ala = Alanine
N-Me-Ala = N-Methylalanine
ABA = 3-Aminobutyric acid
N-Me-ABA = N-Methyl-3-aminobutyric acid
Figure 12: $^1$H NMR spectrum of ancistrocyclinone B (6) in MeOD.
Figure 13: $^{13}$C NMR spectrum of ancistrocyclinone B (6) in MeOD.
Figure 124: DEPT NMR spectrum of ancistrocyclinone B (6) in MeOD.
Figure 15: $^1$H,$^1$H-COSY spectrum of ancistrocyclone B (6) in MeOD.
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Figure 21: ECD spectrum of ancistrocyclinone B (6).
Figure 22: Oxidative degradation products of ancistrocyclinone B (6).
Table 2: Oxidation of 4’-O-demethylancistrocladinium A (8) to 5.

<table>
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<tr>
<th>Entry</th>
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<th>Yield 11 [%]</th>
<th>Yield 5 [%]</th>
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<td>-</td>
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<tr>
<td>2</td>
<td>O₂</td>
<td>-</td>
<td>-</td>
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<tr>
<td>3</td>
<td>Pb(OAc)₄</td>
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</tr>
<tr>
<td>4</td>
<td>Ag₂O</td>
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<td>5</td>
<td>MnO₂</td>
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<tr>
<td>6</td>
<td>H₂O₂</td>
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<tr>
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<td>K₂Cr₂O₄</td>
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<tr>
<td>8</td>
<td>K₃[Fe(CN)₆]</td>
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<td>-</td>
</tr>
<tr>
<td>9</td>
<td>KClO₄</td>
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</table>
Figure 23: Selected NMR data of chinones 11a and 11b: (A) $^1$H and $^{13}$C NMR data ($\delta$ in ppm) of 11a, and (b) of 11b, (c) NOESY (double red arrows) correlations indicative of the relative configurations at the biaryl axes in 11a, and (d) in 11b.

Figure 24: Assignment of the absolute axial configuration of the two atropo-diastereomers of 11 by LC-ECD coupling and by comparison of the LC-ECD spectra of peak A (left) and peak B (right) with the ECD curve of 4'-O-demethylancistrocladinium A (8a).
Figure 25: $^1$H NMR spectrum of chinone 11a (major compound) in MeOD.
Figure 26: $^1$H NMR spectrum of chinone 11b (minor compound) in MeOD.
Figure 27: $^{13}$C NMR spectrum of chinone 11a (major compound) in MeOD.
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Figure 35: $^1$H NMR spectrum of synthetic ancistrocyclinone A (5) in MeOD.
Figure 36: $^{13}$C NMR spectrum of synthetic ancistrocyclinone A (5) in MeOD.
Figure 37: Comparison of the $^1$H NMR spectra of isolated (top) and synthetic (bottom) ancistrocyclinone A (5).
Figure 38: Comparison of the $^{13}$C NMR spectra of isolated (top) and synthetic (bottom) ancistrocyclinone A (5).
Figure 39: Cytotoxic activities of ancistrocladinium A (7a/b) and ancistrocyclinone A (5) against parental drug-sensitive CCRF-CEM leukemia cells and their multi-drug resistant subline, CEM/ADR5000. The compounds were dissolved in DMSO (< 1%) and cell culture medium at concentrations of 0.001, 0.003, 0.01, 0.03, 0.1, 0.3, 1, 3, 10, and 100 μM. Cell viability was assessed by the resazurin assay. Mean values and standard deviation of three independent experiments with each six parallel measurements are shown.