Electronic supplementary information for

The Stereochemistry of Cleistanthane Diterpenoids from

*Phyllanthus emblica*

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Data File: D:\分子量測定\2013-01-24\gca40_TLJ1751_24.lcd

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MSn Logic Mode: OR

Electron ions: both
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Max Results: 800

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4. S4 $^1$H NMR (500 MHz) spectrum of compound 1 in CD$_3$OD
5. $^{13}$C NMR (125 MHz) spectrum of compound 1 in CD$_3$OD
6. S6 HSQC spectrum of compound 1 in CD$_3$OD
7. S7 HMBC spectrum of compound 1 in CD$_3$OD
8. $^1$H-$^1$H COSY spectrum of compound 1 in CD$_3$OD
9. S9 ROESY spectrum of compound 1 in CD$_3$OD
10. S10 HRESIMS of compound 1A
11. S11 $^1$H NMR (600 MHz) spectrum of compound 1A in C$_5$D$_5$N
12.S12 $^{13}$C NMR (150 MHz) spectrum of compound 1A in C$_5$D$_5$N
13. S13 HSQC spectrum of compound 1A in C$_5$D$_5$N
14. **S14 HMBC spectrum of compound 1A in C$_5$D$_5$N**
15. $^1$H-$^1$H COSY spectrum of compound 1A in C$_5$D$_5$N
16. S16 ROESY spectrum of compound 1A in C₅D₅N
17. S17 HRESIMS of compound 2
18. S18 $^1$H NMR (500 MHz) spectrum of compound 2 in CD$_3$OD
19. S19 $^{13}$C NMR (125 MHz) spectrum of compound 2 in CD$_3$OD
20. S20 HSQC spectrum of compound 2 in CD$_3$OD
21. S21 HMBC spectrum of compound 2 in CD$_3$OD
22. S22 $^1$H-$^1$H COSY spectrum of compound 2 in CD$_3$OD
23. S23 ROESY spectrum of compound 2 in CD$_3$OD
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B | 3 | 0 | 0
C | 4 | 0 | 50
N | 3 | 0 | 0
O | 2 | 0 | 30
P | 3 | 0 | 0
S | 2 | 0 | 0
Br | 1 | 0 | 0
I | 3 | 0 | 0
Cl | 1 | 0 | 0

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Use MSn Info: yes
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Max Results: 800

Event #: 2 MS(E-) Ret. Time: 0.240 -> 0.550 - 1.320 -> 2.167 Scan #: 50 -> 112 - 266 -> 436

![Graph of HRESIMS data]
25. S25 $^1$H NMR (600 MHz) spectrum of compound 3 in CD$_3$OD
26. S26 $^{13}$C NMR (150 MHz) spectrum of compound 3 in CD$_3$OD
27. S27 HSQC spectrum of compound 3 in CD$_3$OD
28. S28 HMBC spectrum of compound 3 in CD$_3$OD
29. S29 $^1$H-$^1$H COSY spectrum of compound 3 in CD$_3$OD
30. S30 ROESY spectrum of compound 3 in CD$_3$OD
31. S31 HRESIMS of compound 4
32. S32 $^1$H NMR (600 MHz) spectrum of compound 4 in CD$_3$OD
33. S33 $^{13}$C NMR (150 MHz) spectrum of compound 4 in CD$_3$OD
34. S34 HSQC spectrum of compound 4 in CD$_3$OD
35. S35 HMBC spectrum of compound 4 in CD$_3$OD
36. S36 $^1$H-$^1$H COSY spectrum of compound 4 in CD$_3$OD
37. S37 ROESY spectrum of compound 4 in CD$_3$OD
38. S38 HRESIMS of compound 5

Data File: D:\分子量测定2013-01-24\gca40_TLJ1728_23.lcd

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41. S41 HSQC spectrum of compound 5 in CD₃OD
42. S42 HMBC spectrum of compound 5 in CD$_3$OD
43. S43 $^1H-^1H$ COSY spectrum of compound 5 in CD$_3$OD
44. S44 ROESY spectrum of compound 5 in CD$_3$OD
45. S45 HRESIMS of compound 6
46. S46 $^1$H NMR (600 MHz) spectrum of compound 6 in CD$_3$OD
47. $^{13}$C NMR (150 MHz) spectrum of compound 6 in CD$_3$OD
48. S48 HSQC spectrum of compound 6 in CD$_3$OD
49. S49 HMBC spectrum of compound 6 in CD$_3$OD
50. S50 $^1$H-$^1$H COSY spectrum of compound 6 in CD$_3$OD
51. S51 ROESY spectrum of compound 6 in CD$_3$OD
52. S52 ESI MS spectrum of 1B

YLJ1651-1 19 (0.376) Cm (12:23-2:4x10.000) 1: MS2 ES+
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53. S53 $^1$H NMR spectrum of (S)-MTPA ester derivative 1s of 1B (800 MHz, CDCl$_3$)
S54 1H-1H COSY spectrum of (S)-MTPA ester derivative 1s of 1B (800 MHz, CDCl3)
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58. S58 ROESY spectrum of (R)-MTPA ester derivative 1r of 1B (800 MHz, CDCl₃)
59. S59 ECD calculations of compound 1A

Figure 3. DFT optimized conformers of the aglycon of 3R,5S,10R-phyllanembloid A (1A) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.
Figure 4. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon of 3R,5S,10R- phyllanembloid A (1A), with Gaussian band shape 0.3ev.
S60 ECD calculations of compound 1

Figure 5. DFT optimized conformers of 3R,5S,10R- phyllanembloid A (1) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.
Figure 6. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of 3R,5S,10R-phyllanembloid A (1), with Gaussian band shape 0.3ev.
61. S61 ECD calculations of compound 3

Figure 7. DFT optimized conformers of the aglycon of 3S,5S,10R- phyllanembloid C (3) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.
Figure 8. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon of 3S,5S,10R- phyllanembloid C (3), with Gaussian band shape 0.5ev.
62. S62 ECD calculations of compound 4

Figure 9. DFT optimized conformers of the aglycon of 3R,10R- phyllanembloid D (4) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.
Figure 10. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon of 3R, 10R- phyllanembloid D (4), with Gaussian band shape 0.3eV.
63. S63 ECD calculations of compound 5

Figure 11. DFT optimized conformers of the aglycon of \(3R,4R,5S,10R\)-phyllanembloid E (5) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.

Figure 12. TDDFT calculated ECD spectra at B3LYP/6-311G(d, p) level in methanol (IEFPCM) for the low energy conformers of the aglycon of \(3R,4R,5S,10R\)-phyllanembloid E (5), with Gaussian band shape 0.5ev.
64. S64 OR calculations of compound 6

Figure 13. DFT optimized conformers of 3R,4R,5S,9R,10S,12R,13R- phyllanembloid F (6) at B3LYP/6-311G(d, p) level in methanol (IEFPCM), with free energies calculated at the same level and Boltzmann distribution at 298 K estimated thereof.

Table 1. Calculated optical rotations of conformers of 3R,4R,5S,9R,10S,12R,13R- phyllanembloid F (6)

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Optical rotations were calculated with the basis set B3LYP 6-311G (++2d, p) at gas phase using the optimized conformers at B3LYP 6-311G (2d, p).