Supplementary Materials

Figure S1. ^{1}H-NMR spectrum of lysicamine (**1**).

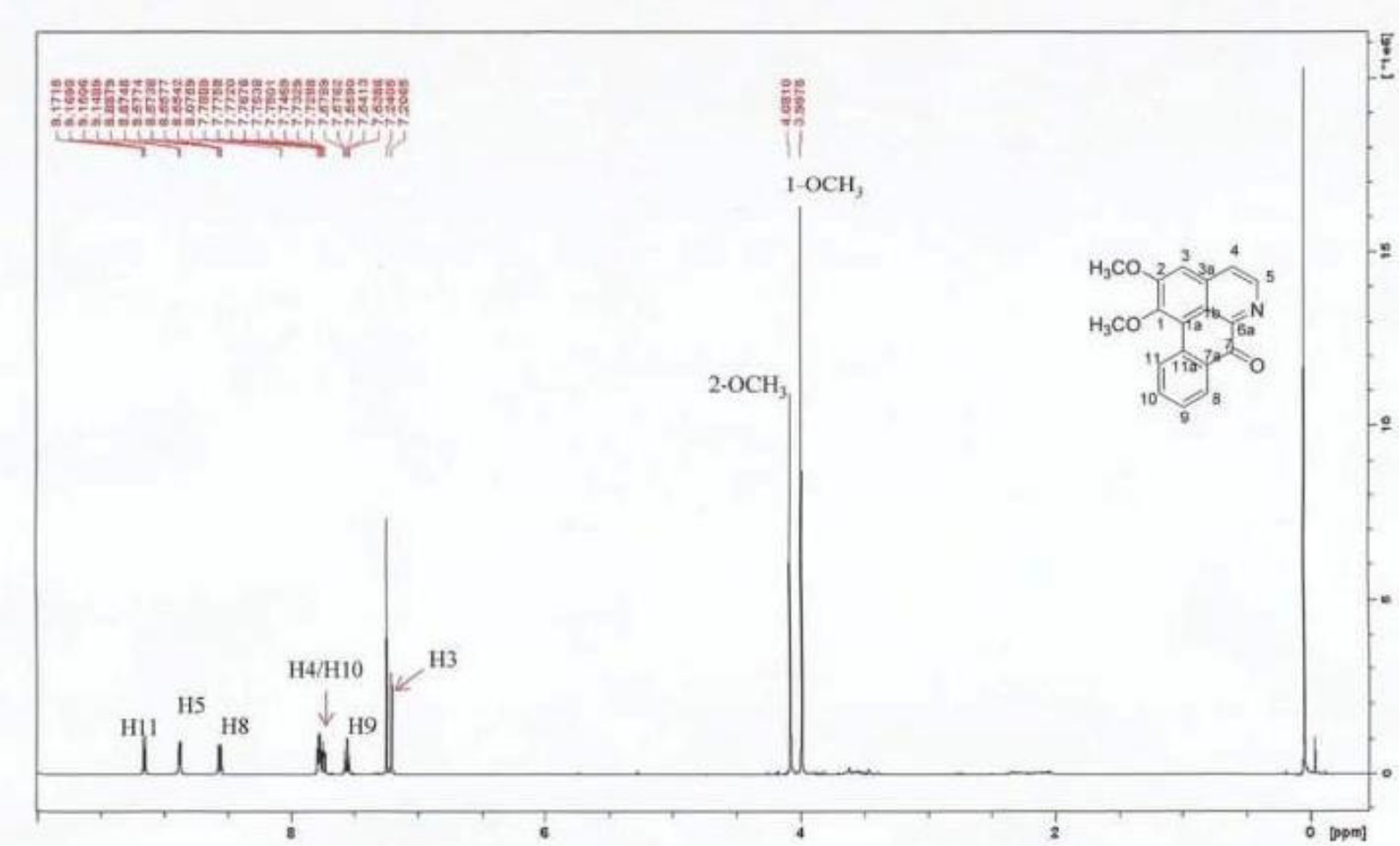


Figure S2. ^{13}C-NMR spectrum of lysicamine (**1**).

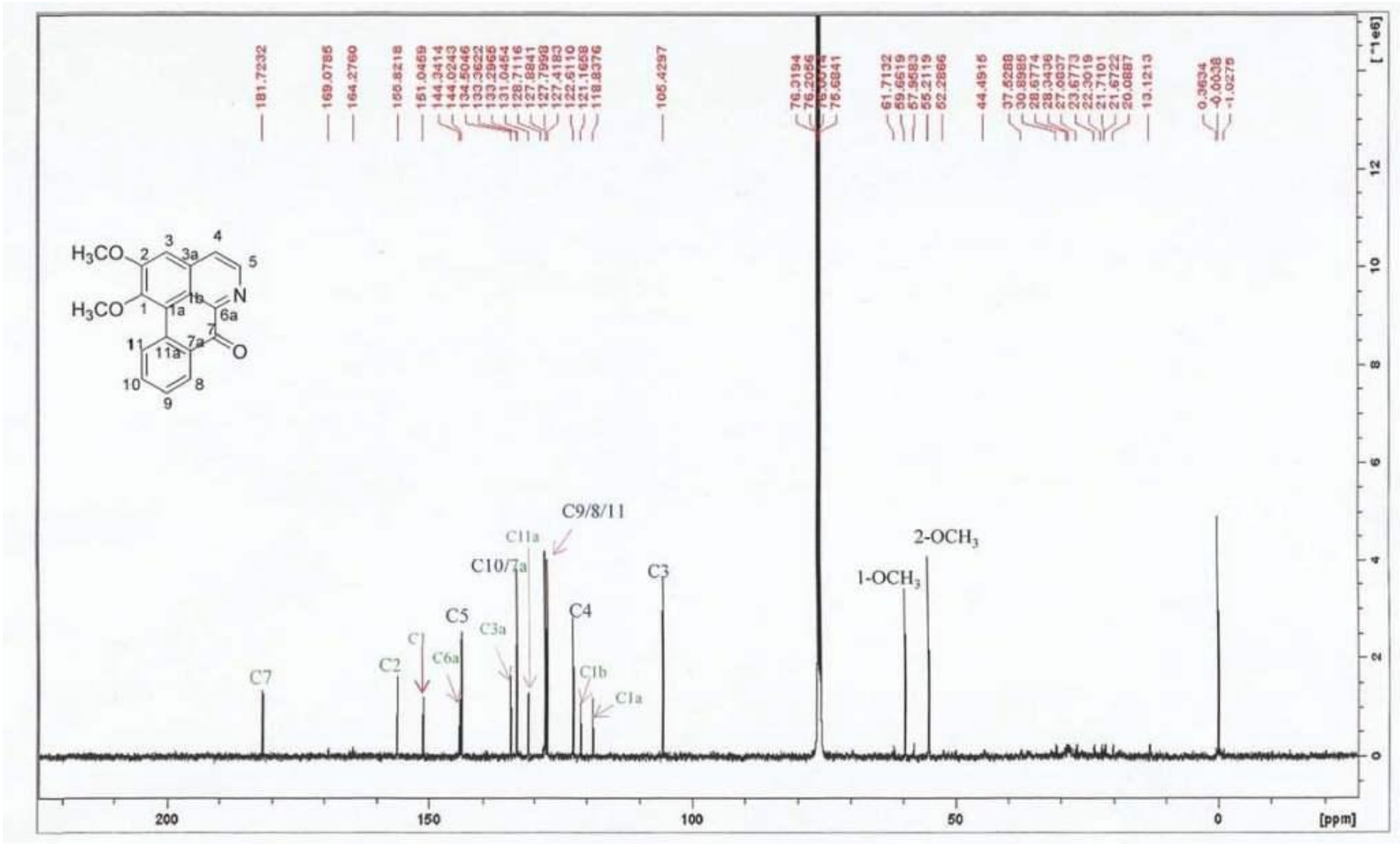
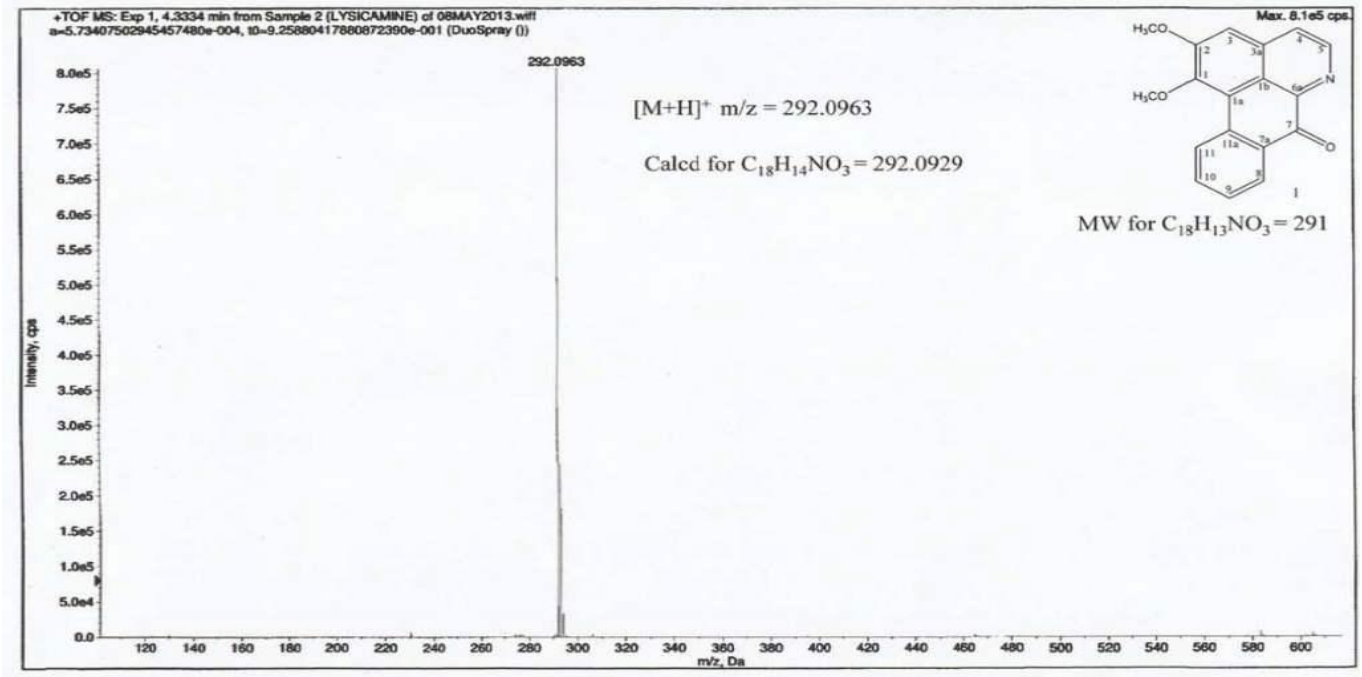


Figure S3. LCMS Triple TOF-MS spectrum of lysicamine (**1**).



Lysicamine, (**1**): $C_{18}H_{13}NO_3$, yellow amorphous solid. $[\alpha]_D^{29}$ = −25 (c= 0.00008, $CHCl_3$). LCMS Triple TOF *m/z*: 292.0963 $[M+H]^+$. (calcd for $C_{18}H_{14}NO_3$, 292.0929). ^{1}H NMR (400 MHz, CD_3OD, δ, ppm, *J*/Hz): 7.21 (1H, s, H-3), 7.78 (1H, d, *J* = 5.2, H-4), 8.88 (1H, d, *J* = 5.2, H-5), 8.57 (dd, *J* = 7.8, 1.4, H-8), 7.75 (1H, dt, *J* = 8.3, H-9), 7.56 (1H, dt, *J* = 8.0, 1.1, H-10), 9.16 dd (1H, *J* = 8.4, 0.7, H-11), 4.00 (3H, s, 1-OMe), 4.08 (3H, s, 2-OMe). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 151.0 (C-1), 118.8 (C-1a), 121.2 (C-1b), 155.8 (C-2), 105.4 (C-3), 134.5 (C-3a), 122.6 (C-4), 144.0 (C-5), 144.3 (C-6a), 181.7 (C-7), 133.3 (C-7a), 127.8 (C-8), 127.9 (C-9), 133.4 (C-10), 127.4 (C-11), 131.04 (C-11a), 59.7 (1-OCH_3), 55.2 (2-OCH_3).

Figure S4. ^{1}H-NMR spectrum of litsericinone (**2**).

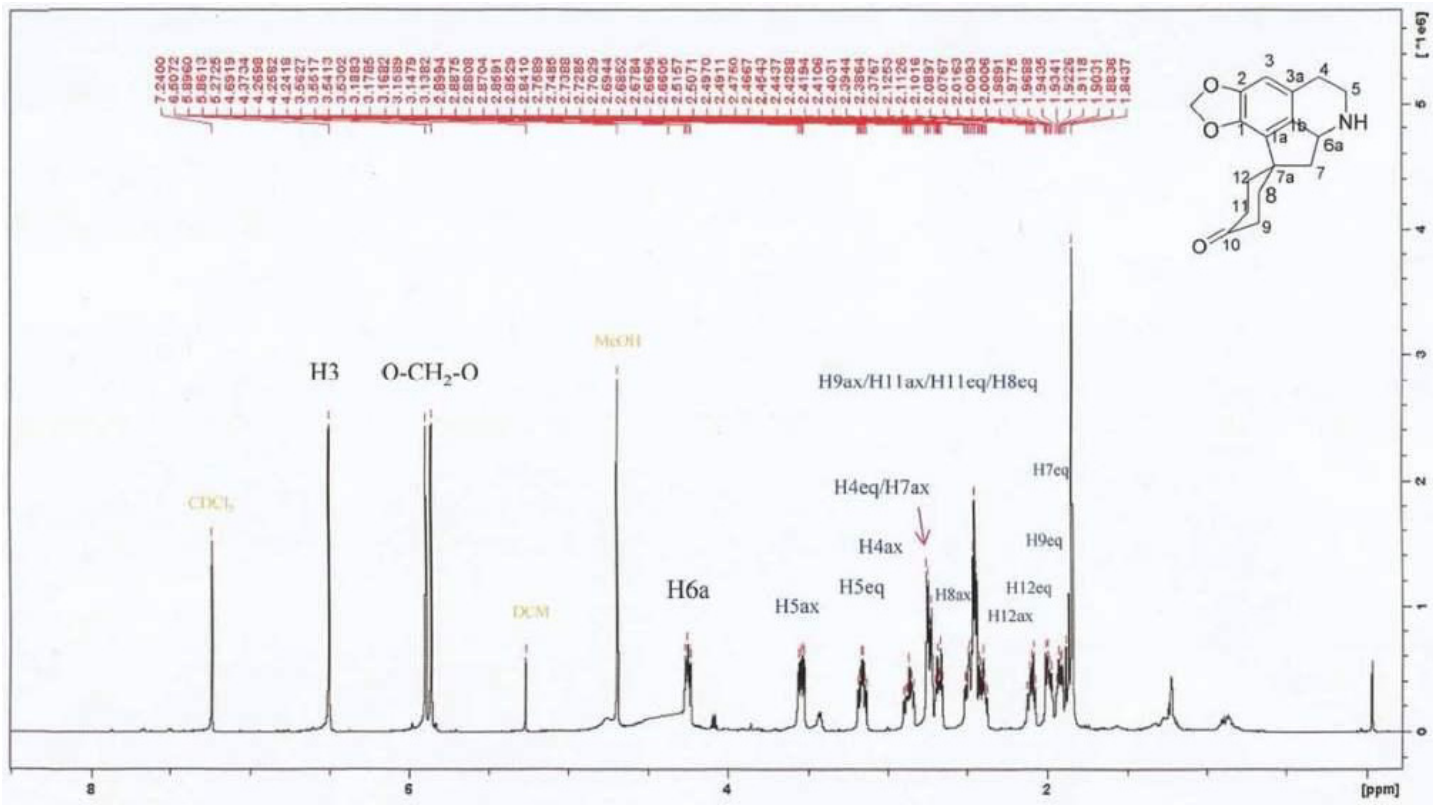


Figure S5. ^{13}C-NMR spectrum of litsericinone (**2**).

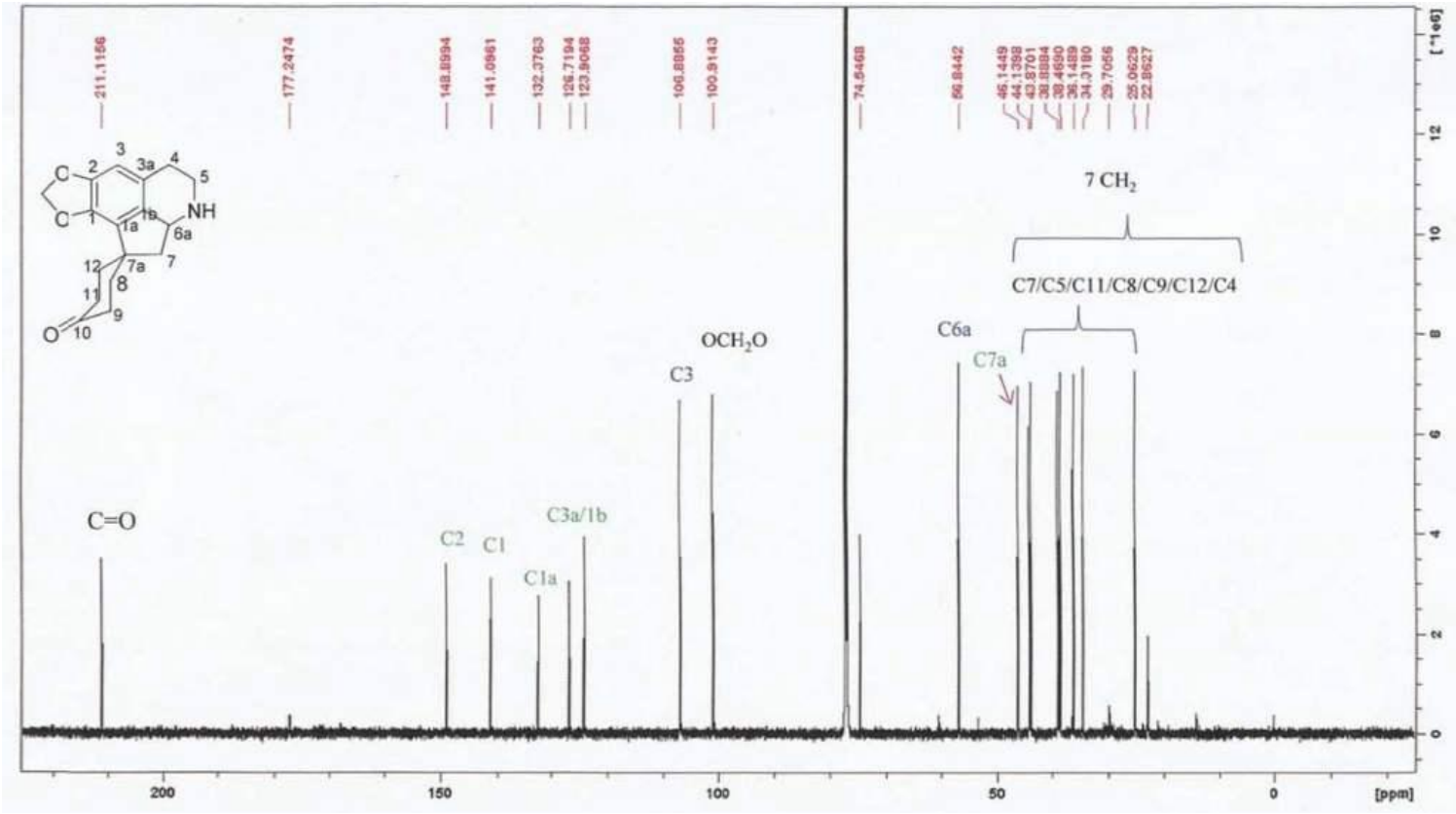


Figure S6. DEPT 135-NMR spectrum of litsericinone (**2**).

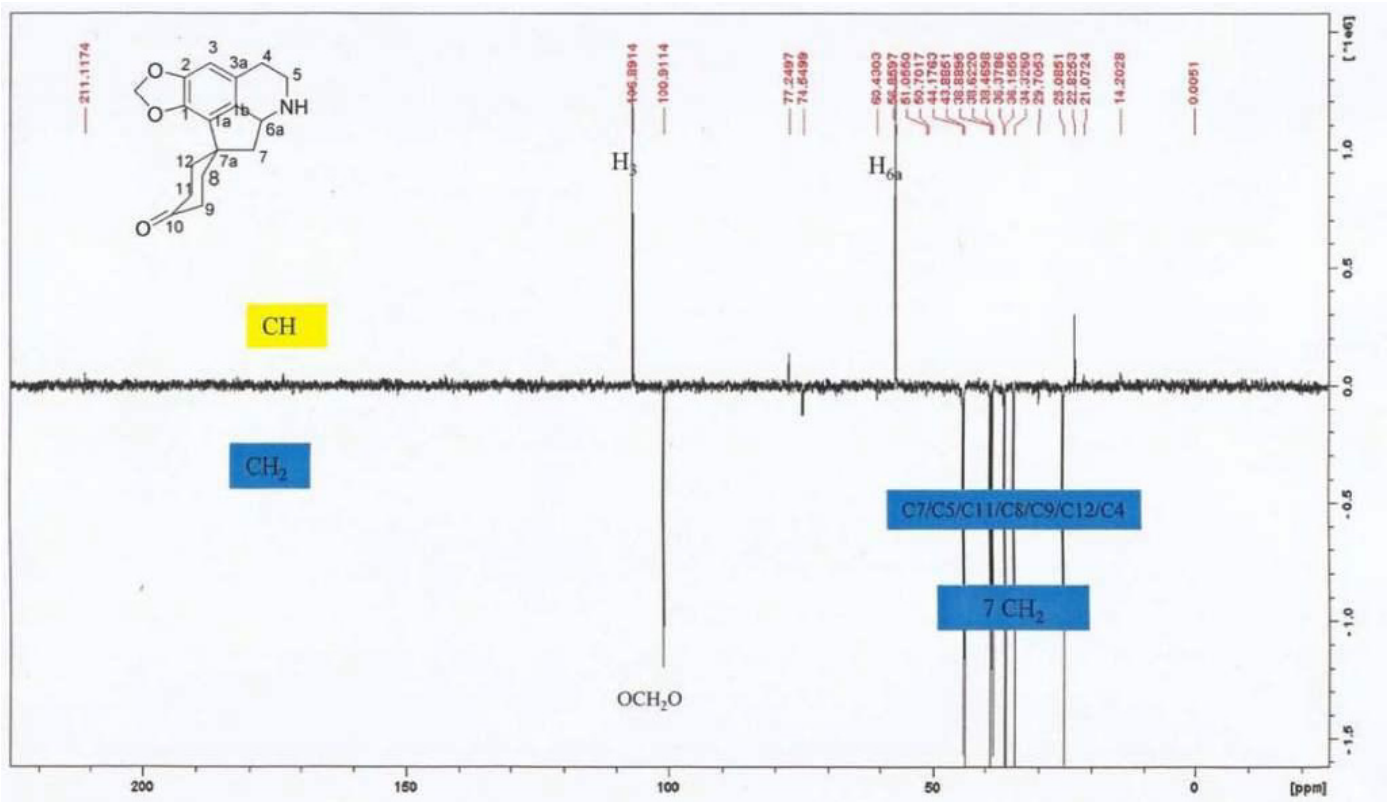


Figure S7. ^{1}H-^{1}H COSY-NMR spectrum of litsericinone (**2**).

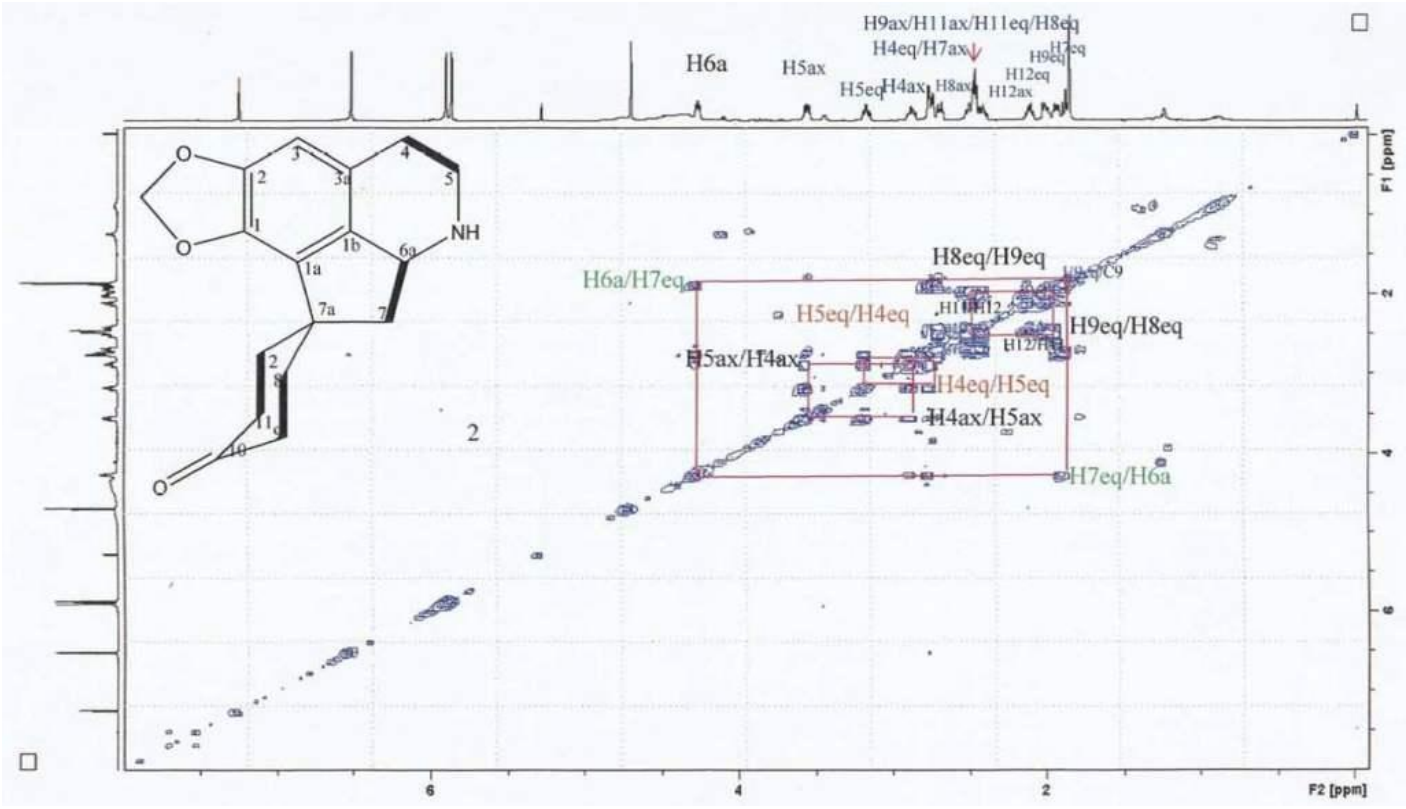


Figure S8. ^{1}H-^{13}C HSQC-NMR spectrum of litsericinone (**2**).

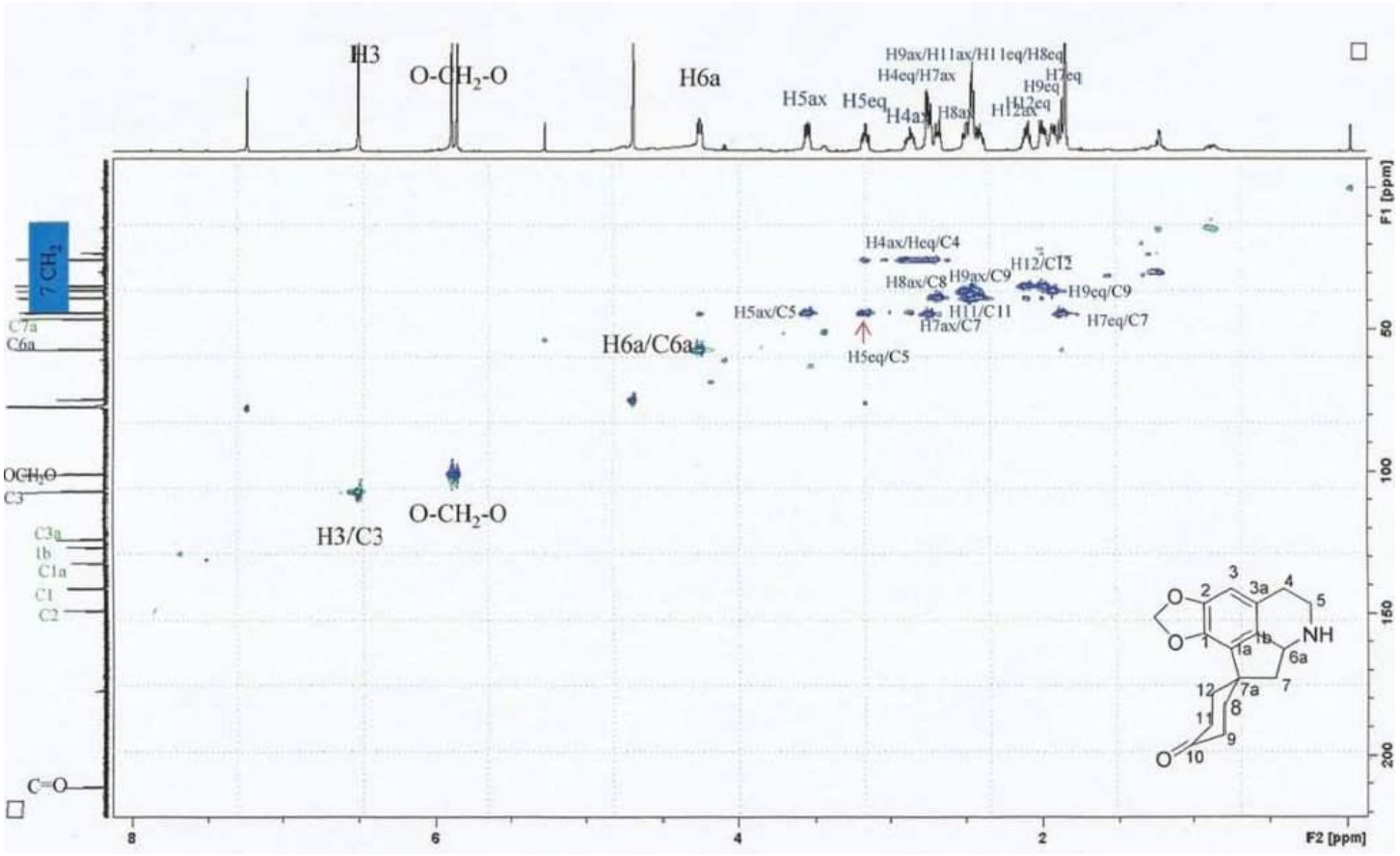


Figure S9. ^{1}H-^{13}C HMBC-NMR spectrum of litsericinone (**2**).

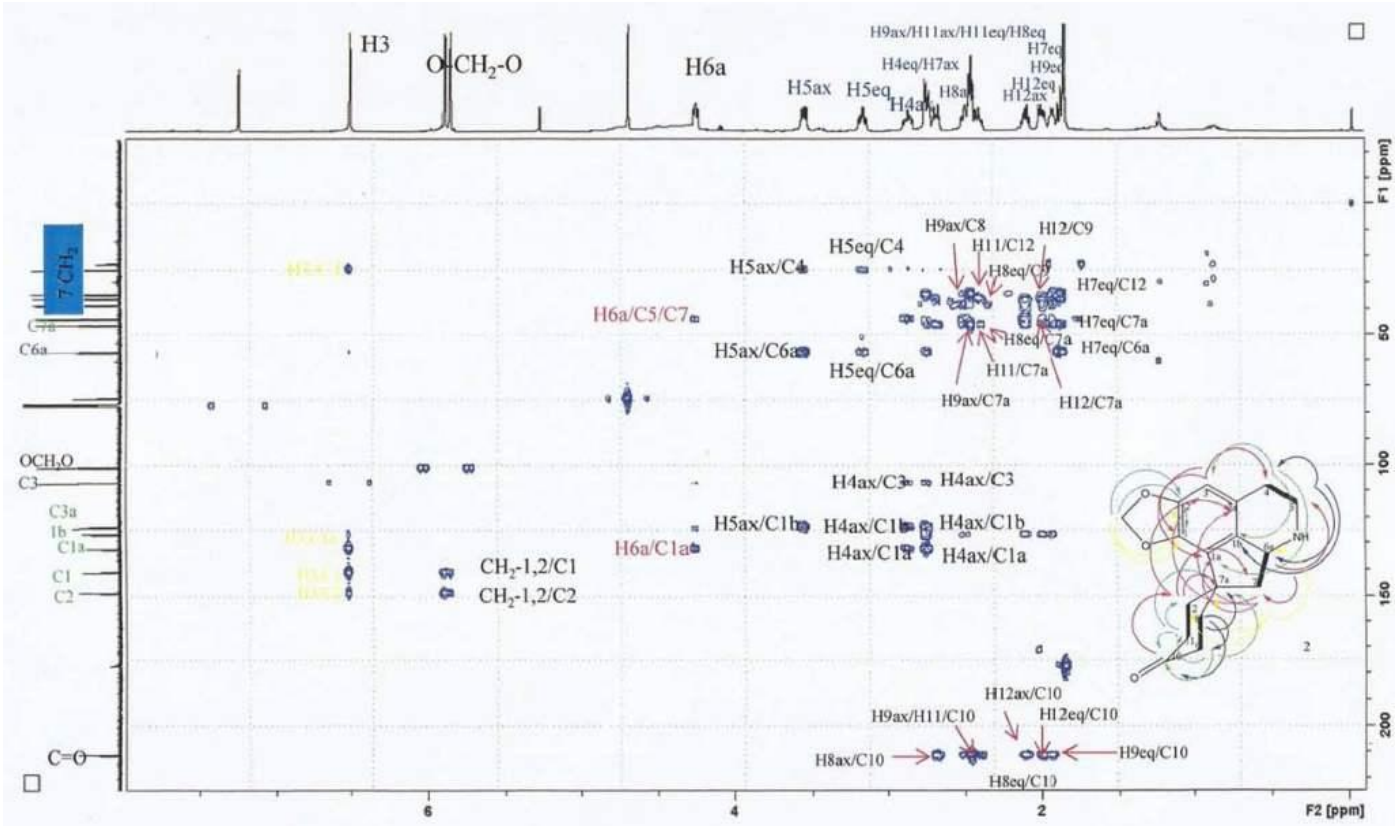
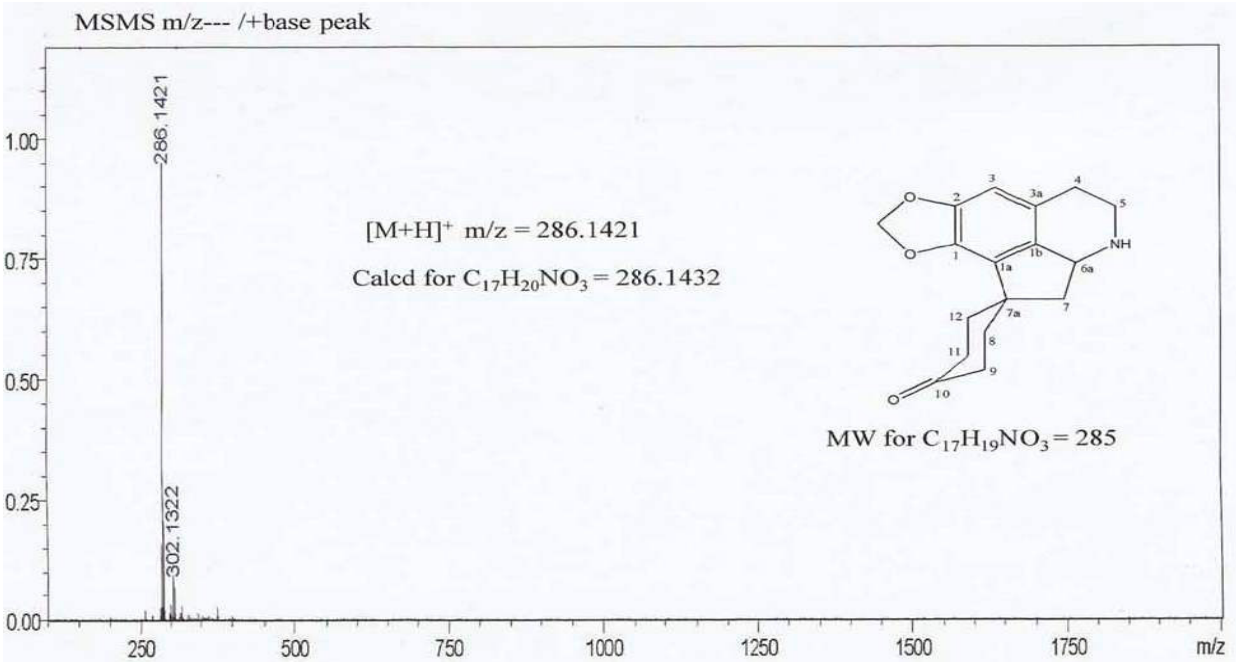


Figure S10. LCMS IT TOF-MS spectrum of litsericinone (**2**).



Litsericinone (**2**): $C_{17}H_{19}NO_3$, yellow amorphous; $[\alpha]_D^{29}$ = −25 (c=0.00004, $CHCl_3$). LCMS-IT-TOF (Shimadzu), ESI *m/z*: 286.1421 $[M+H]^+$ (calcd for $C_{17}H_{20}NO_3$, 286.1432). ^{1}H NMR (600 MHz, CD_3OD, δ, ppm, *J*/Hz): 6.51 (1H, s, H-3), 2.87 (1H, m, H-4β), 2.75 (1H, m, H-4α), 3.55 (1H, m, H-5β), 3.16 (1H, m, H-5α), 4.26 (1H, dd, *J* = 6.9, 9.8 Hz, H-6a), 2.73 (1H, m, H-7β), 1.87 (1H, m, H-7α), 2.68 (1H, m, H-8β), 2.41 (1H, m, H-8α), 2.50 (1H, m, H-9β), 1.91 (1H, m, H-9 α), 2.46 (1H, m, H-11β), 2.45 (1H, m, H-11α), 2.10 (1H, m, H-12β), 2.00 (1H, m, H-12α), 5.89 (1H, d, *J*=1.3 Hz (O-CH_2-O), 5.86 (1H, d, *J*=1.3 Hz (O-CH_2-O). ^{13}C NMR (150 MHz, CD_3OD, δ, ppm): 148.9 (C-1), 132.4 (C-1a), 123.9 (C-1b), 141.1 (C-2), 106.9 (C-3), 126.7 (C-3a), 25.1 (C-4), 43.9 (C-5), 56.8 (C-6a), 44.1 (C-7), 46.2 (C-7a), 38.5 (C-8), 36.2 (C-9), 211.1 (C-10), 38.9 (C-11), 34.3 (C-12), 100.9 (O-CH_2-O).

Figure S11. ^{1}H-NMR spectrum of 8,9,11,12-tetrahydromecambrine (**3**).

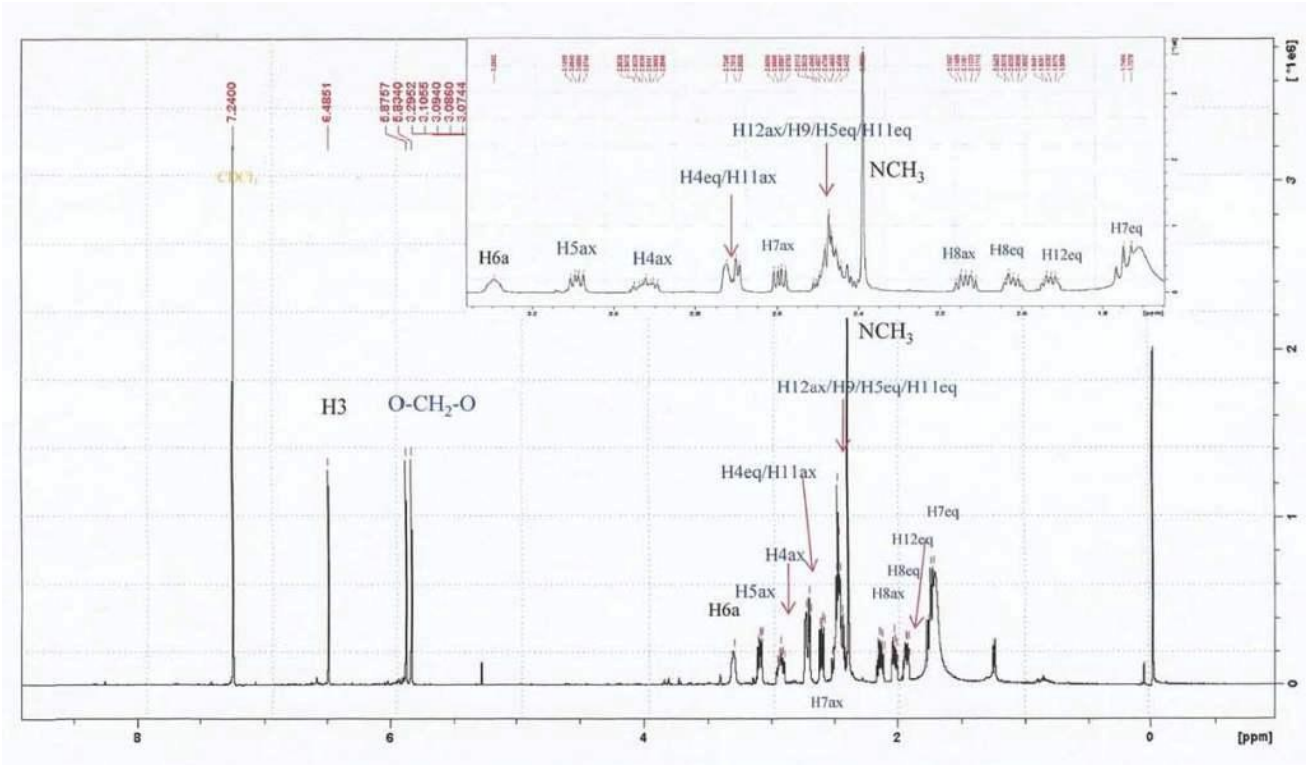


Figure S12. ^{13}C-NMR spectrum of 8,9,11,12-tetrahydromecambrine (**3**).

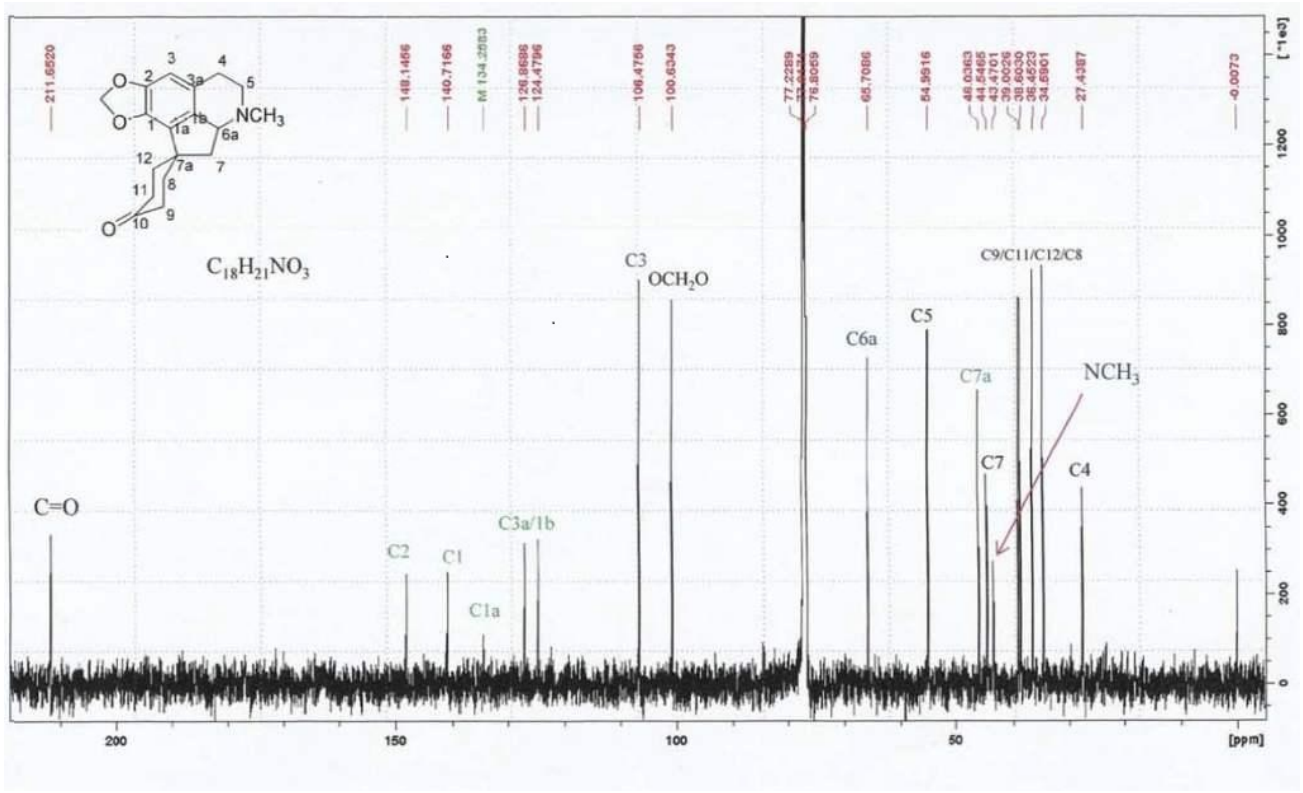


Figure S13. DEPT 135-NMR spectrum of 8,9,11,12-tetrahydromecambrine (**3**).

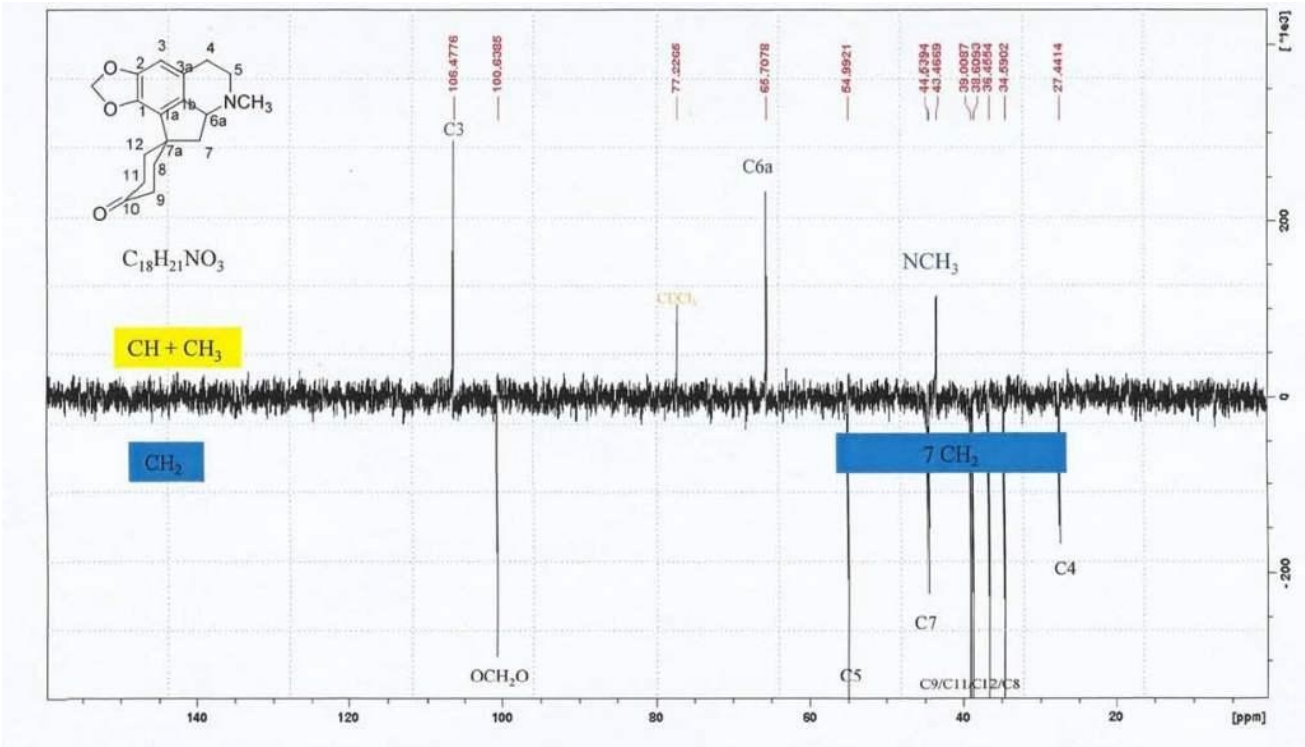


Figure S14. ^{1}H-^{1}H COSY-NMR spectrum of 8,9,11,12-tetrahydromecambrine (**3**).

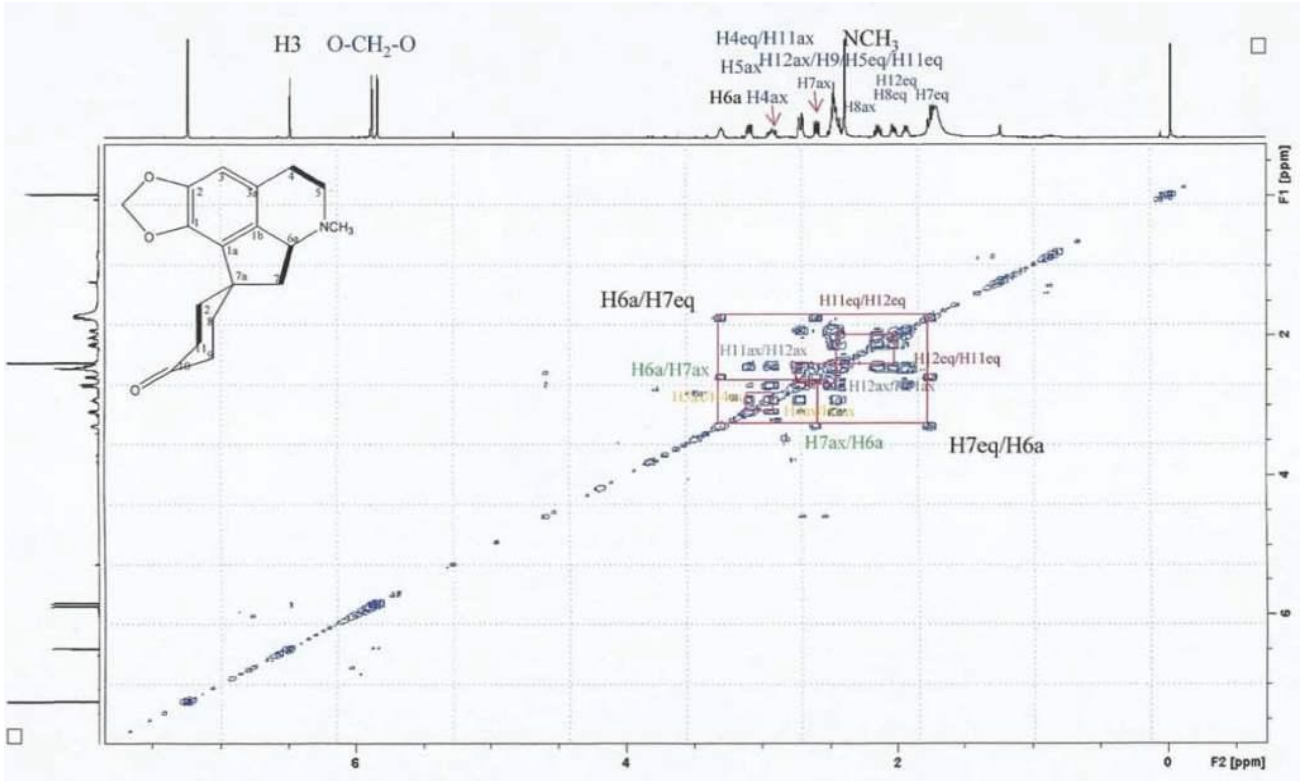


Figure S14.1. ^{1}H-^{1}H COSY-NMR spectrum of 8,9,11,12-tetrahydromecambrine (**3**).

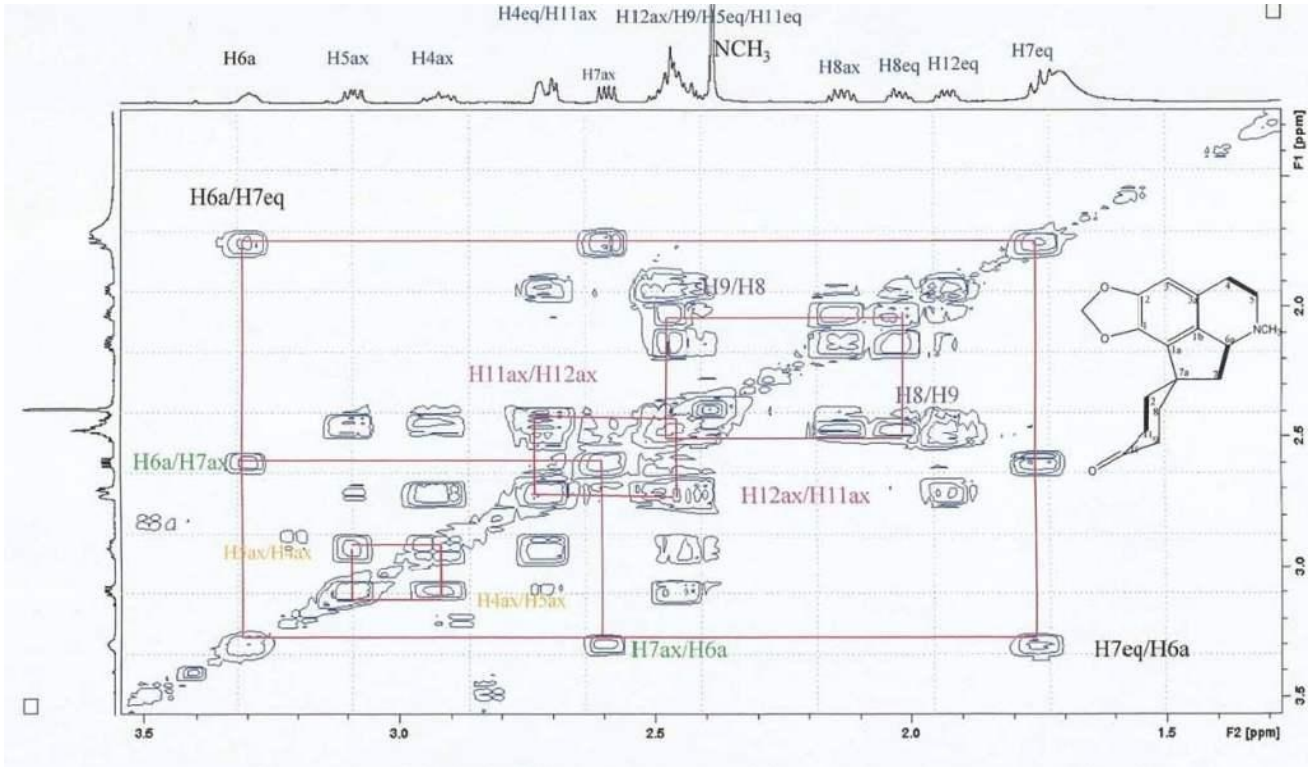


Figure S15. ^{1}H-^{13}C HSQC-NMR spectrum of 8,9,11,12-tetrahydromecambrine (**3**).

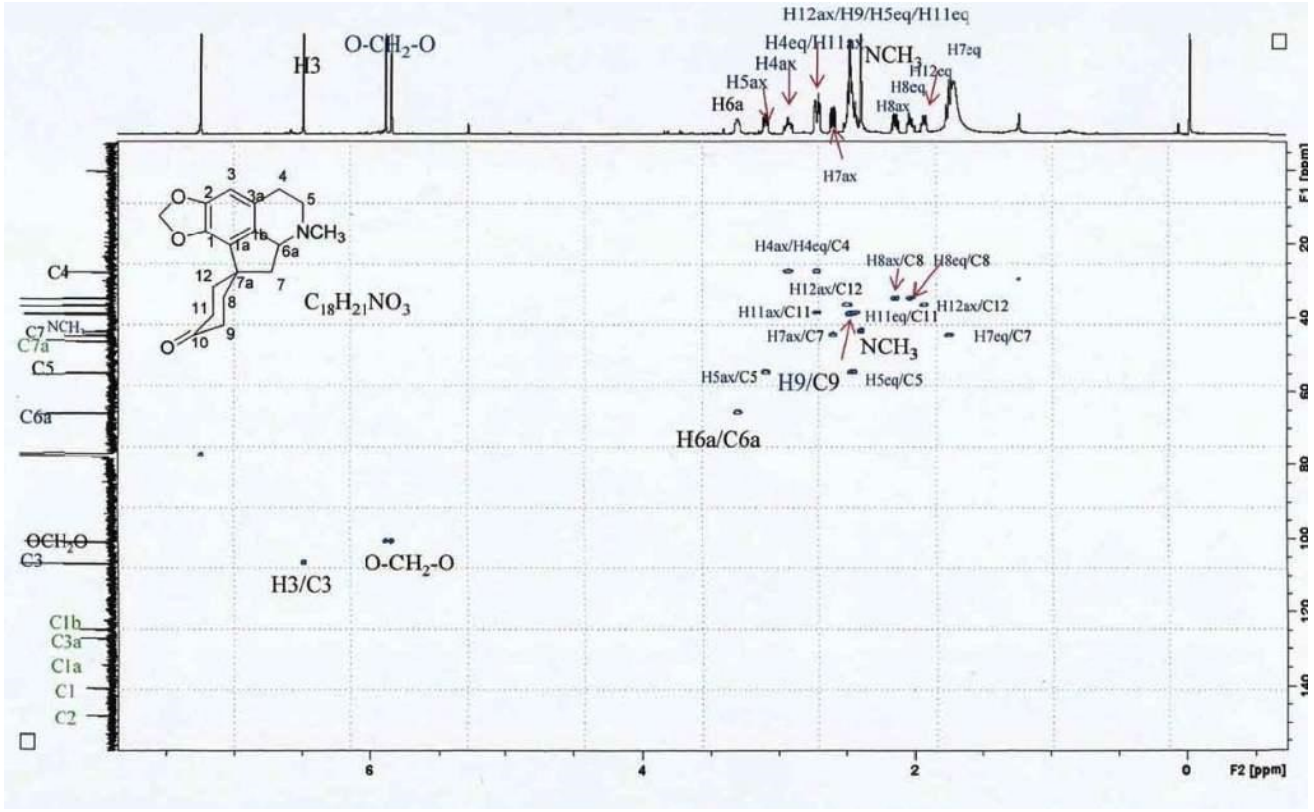


Figure S16. ^{1}H-^{13}C HMBC-NMR spectrum of 8,9,11,12-tetrahydromecambrine (**3**).

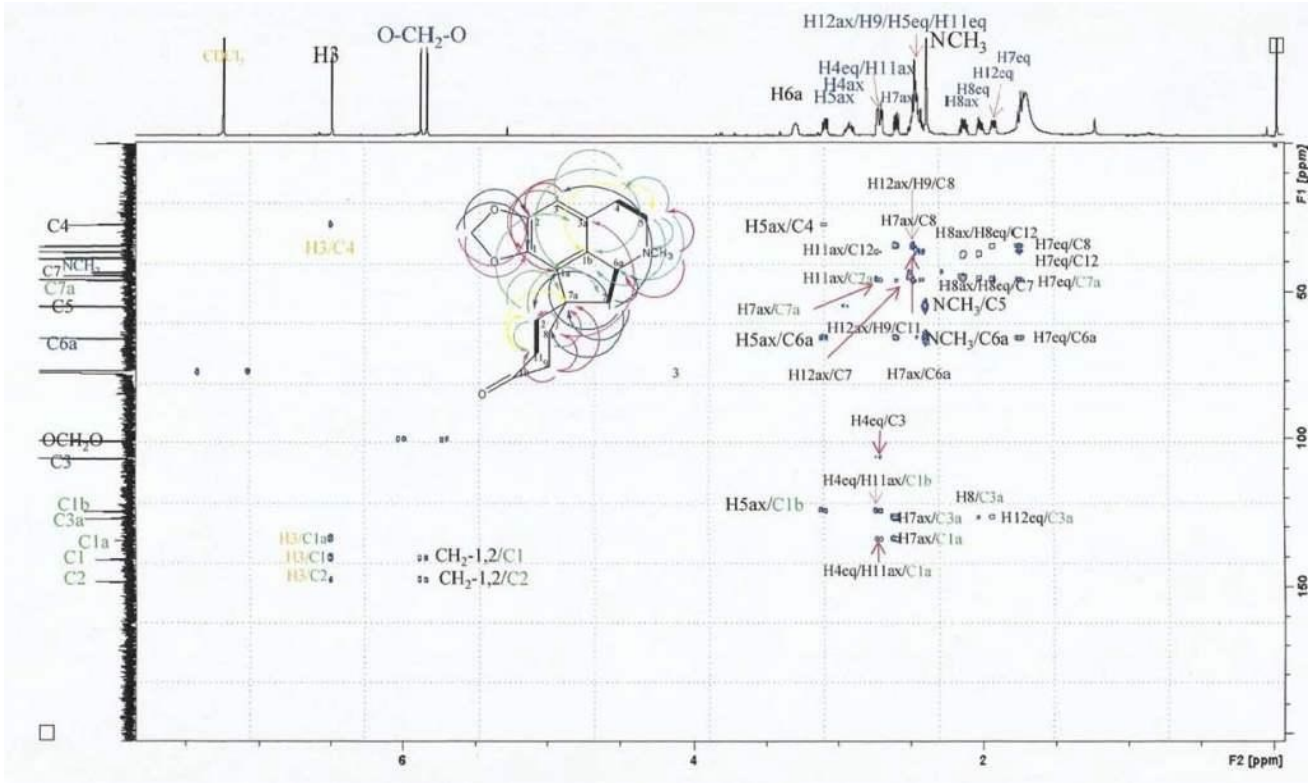
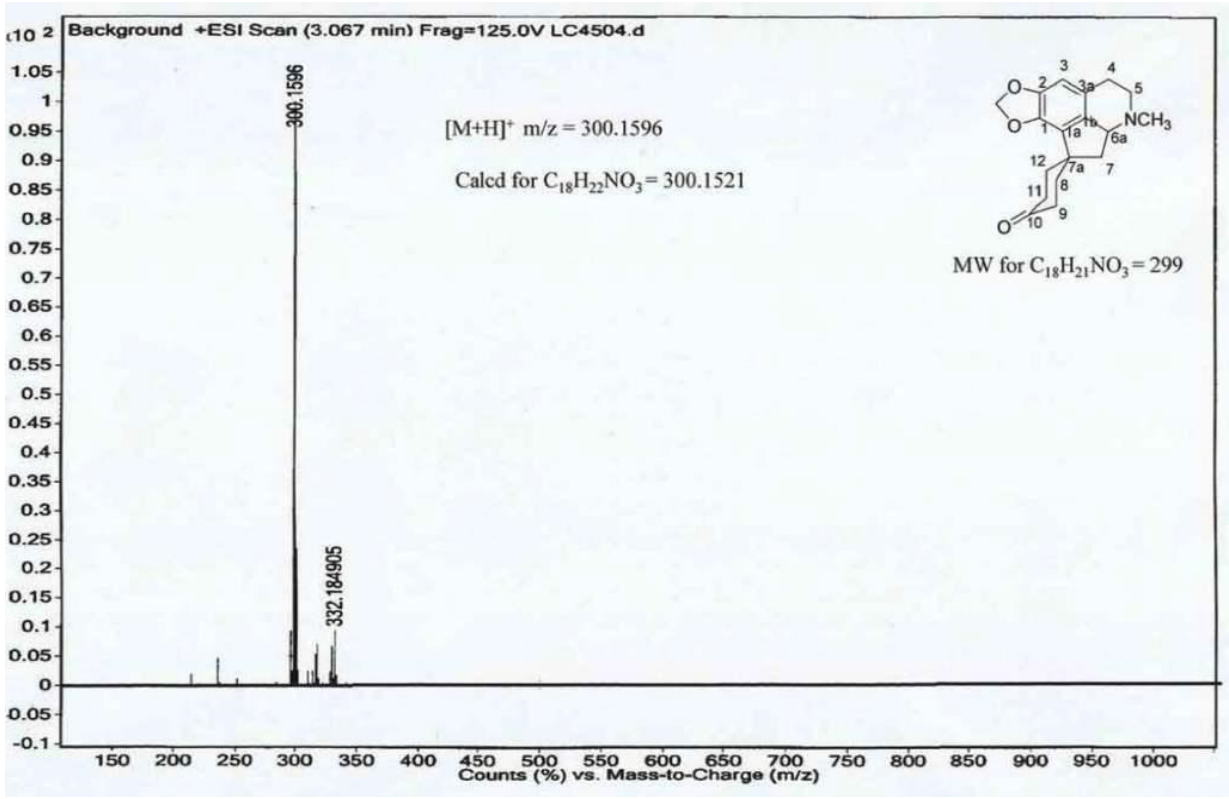


Figure S17. ESI-MS spectrum of 8,9,11,12-tetrahydromecambrine (**3**).



8,9,11,12-tetrahydromecambrine (**3**): $C_{18}H_{21}NO_3$, yellow amorphous solid. $[\alpha]_D^{29}$ = −25 (c=0.00004, $CHCl_3$); UV: λ_{max} (MeOH) 203.0 nm; IR ($CHCl_3$) υ_{max} 2928.30, 1712.80, 1470.92, 1254.45, 1044.56, 754.55 cm^{-1}. LCMS-IT-TOF *m/z*: 300.1596 $[M+H]^+$, (calcd for $C_{18}H_{22}NO_3$, 300.1521). ^1H NMR (600 MHz, CD_3OD, δ, ppm, *J*/Hz): 6.49 (1H, s, H-3), 2.92 (1H, m, H-4ax), 2.72 (1H, m, H-4eq), 3.09 (1H, m, H-5ax), 2.45 (1H, m, H-5eq), 3.30 (1H, br s, H-6a), 2.59 (1H, m, H-7ax), 1.75 (1H, m, H-7eq), 2.14 (1H, m, H-8ax), 2.02 (1H, m, H-8eq), 2.47 (1H, m, H-9ax,eq), 2.70 (1H, m, H-11ax), 2.43 (1H, m, H-11eq), 2.50 (1H, m, H-12ax), 1.93 (1H, m, H-12eq), 5.88 (1H, d, *J*=1.2, O-CH_2-O), 5.83 (1H, d, *J*=1.2, O-CH_2-O). ^{13}C NMR (150 MHz, CD_3OD, δ, ppm): 140.7 (C-1), 134.2 (C-1a), 124.5 (C-1b), 148.2 (C-2), 106.5 (C-3), 126.9 (C-3a), 27.4 (C-4), 55.0 (C-5), 65.7 (C-6a), 44.5 (C-7), 46.0 (C-7a), 34.6 (C-8), 39.0 (C-9), 211.7 (C-10), 38.6 (C-11), 36.5 (C-12), 100.6 (O-CH_2-O).

Figure S18. ^{1}H-NMR spectrum of hexahydromecambrine A (**4**).

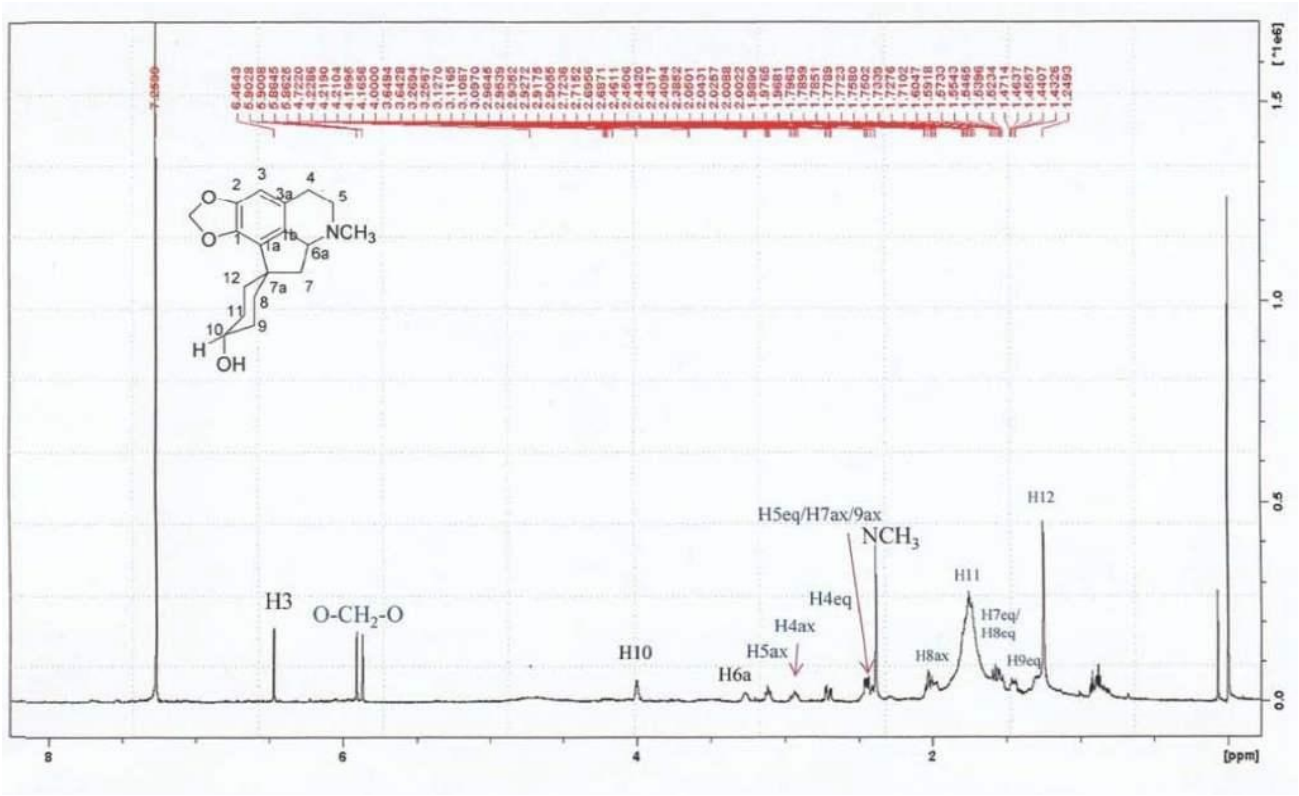


Figure S19. ^{13}C-NMR spectrum of hexahydromecambrine A (**4**).

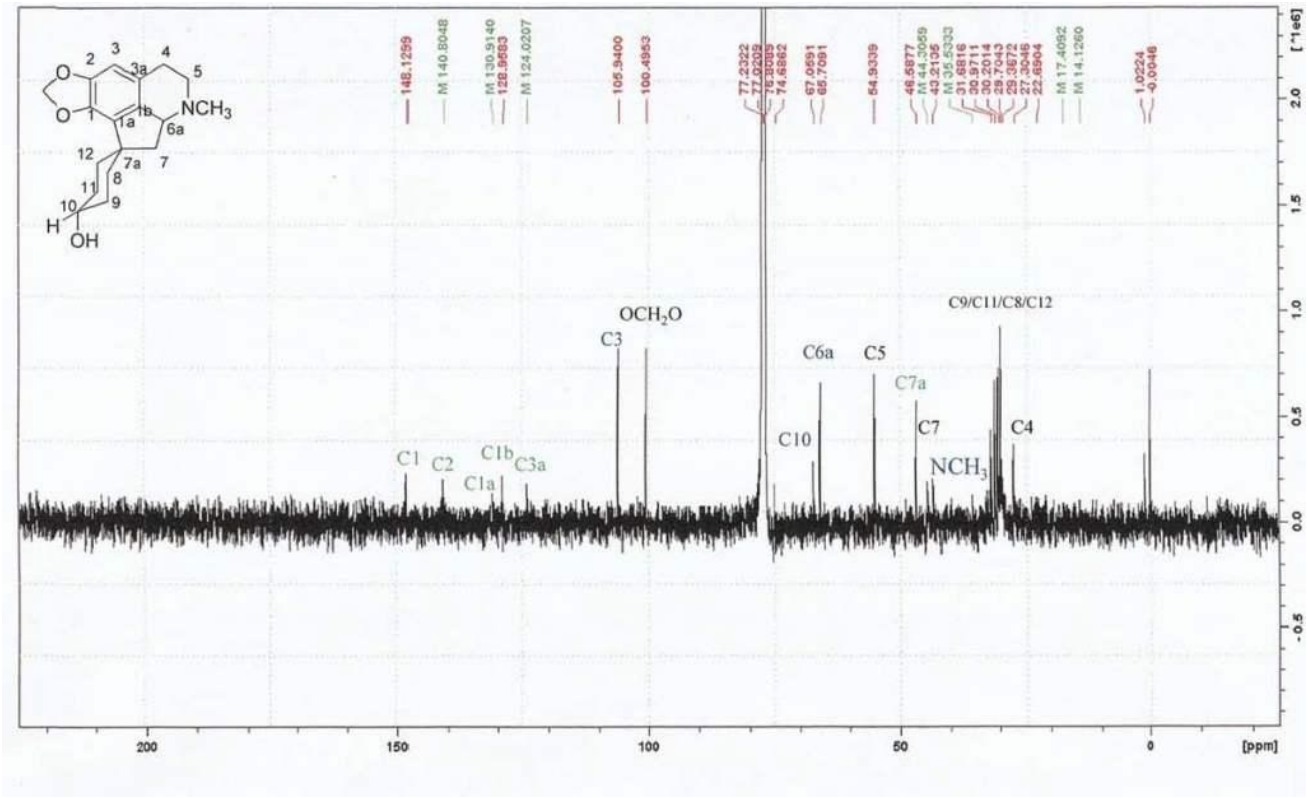


Figure S20. DEPT 135-NMR spectrum of hexahydromecambrine A (**4**).

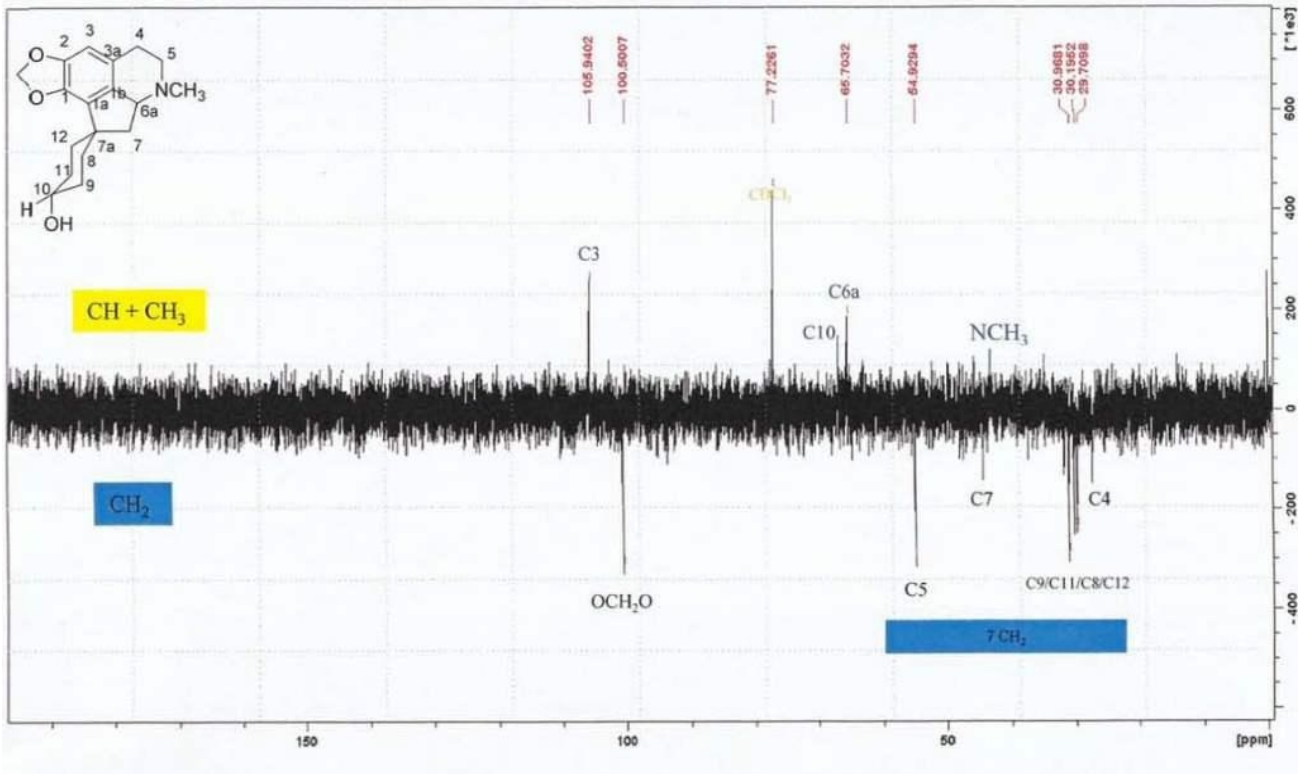


Figure S21. ^{13}C and DEPT 135 -NMR spectrum of hexahydromecambrine A (**4**).

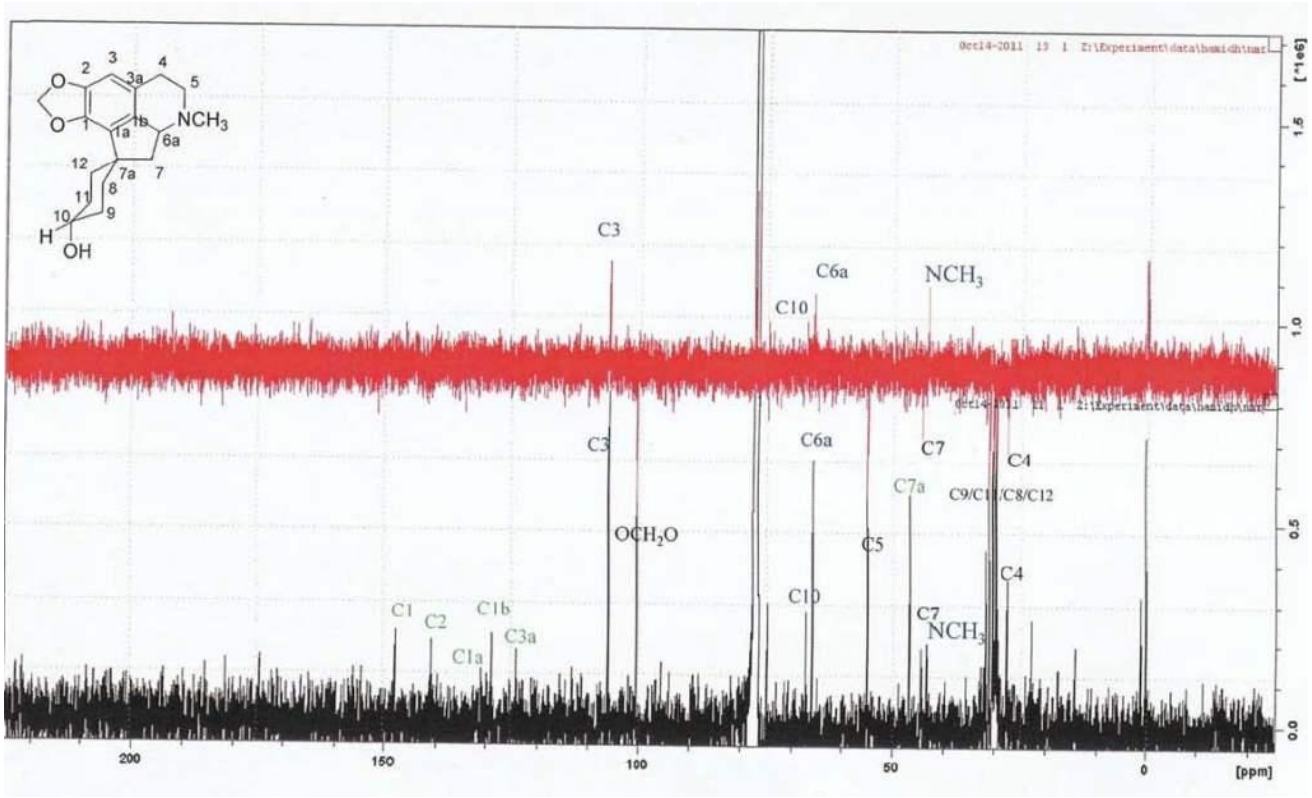


Figure S22. ^{1}H-^{1}H COSY-NMR spectrum of hexahydromecambrine A (**4**).

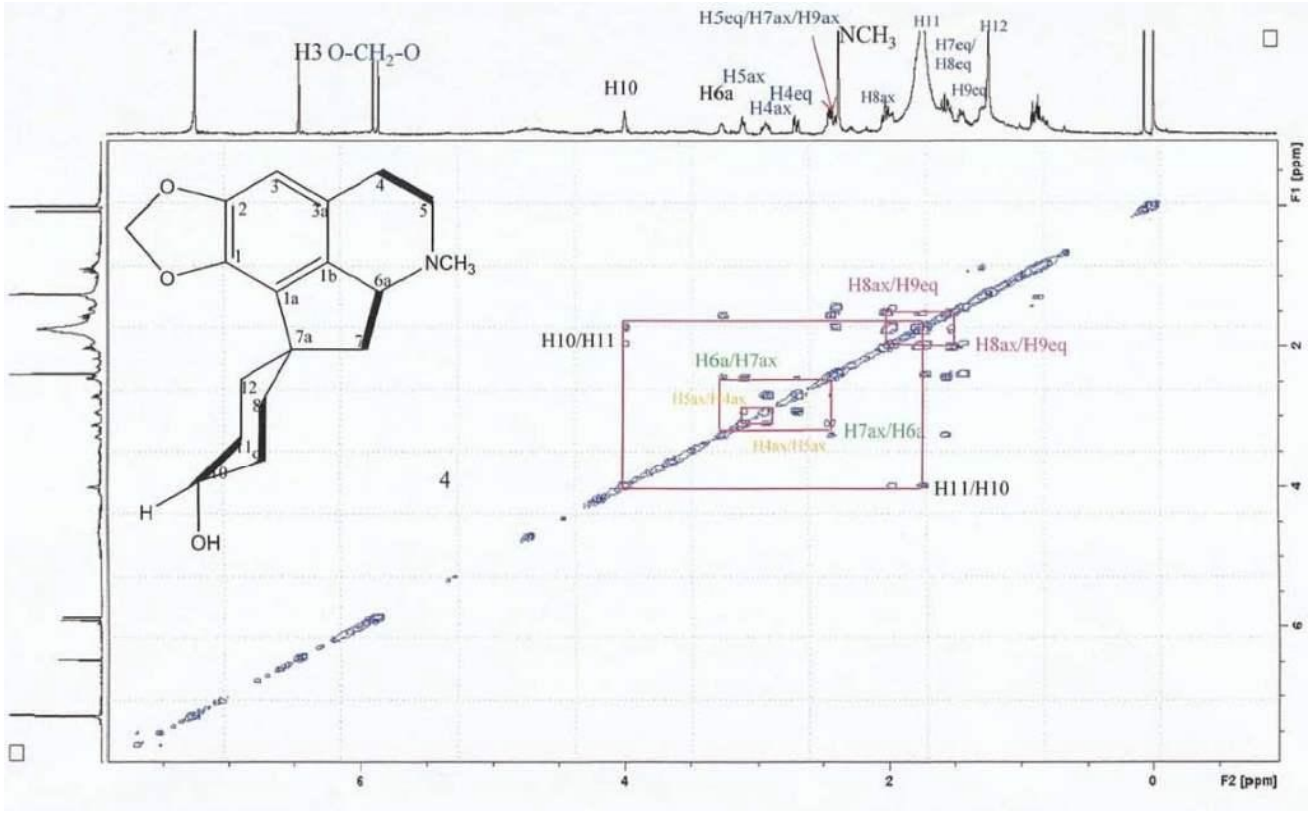


Figure S23. ^{1}H-^{13}C HSQC-NMR spectrum of hexahydromecambrine A (**4**).

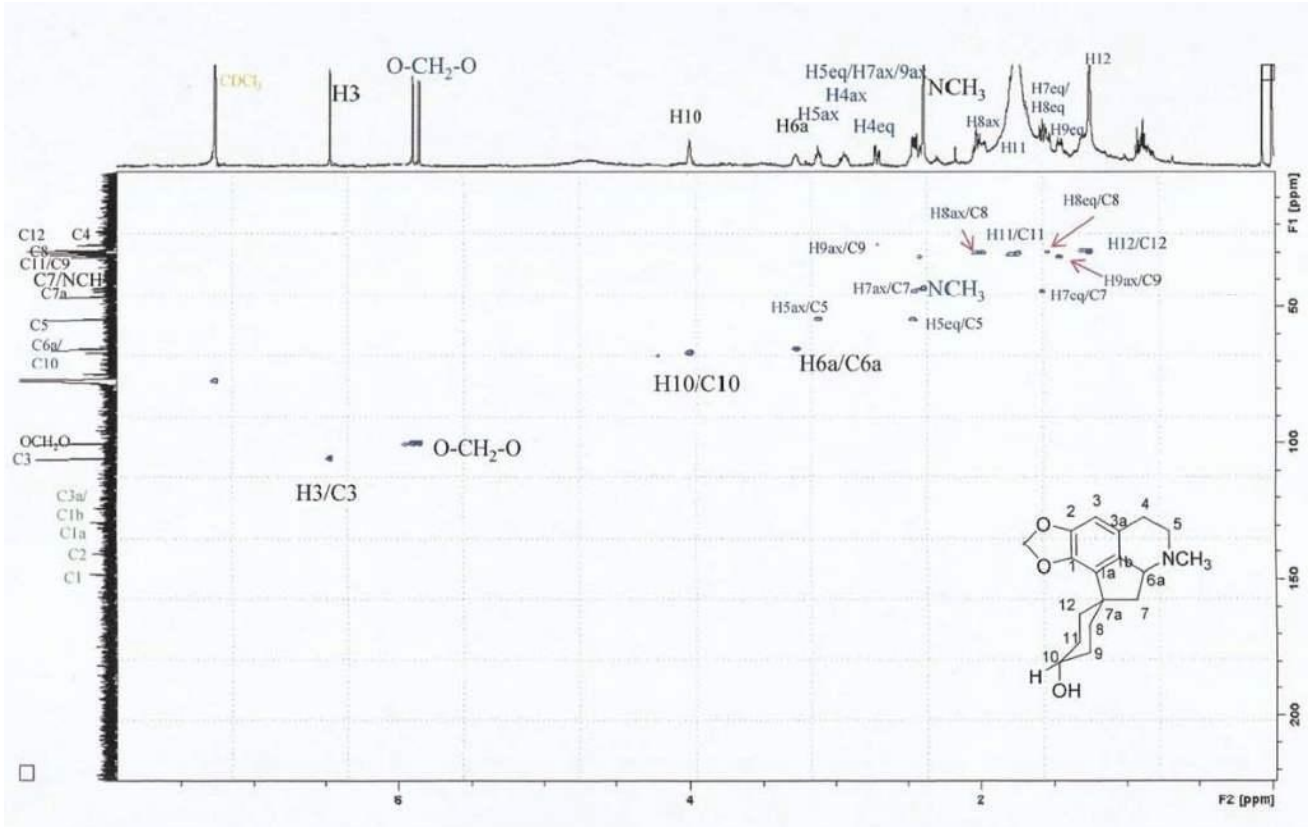


Figure S24. ^{1}H-^{13}C HMBC-NMR spectrum of hexahydromecambrine A (**4**).

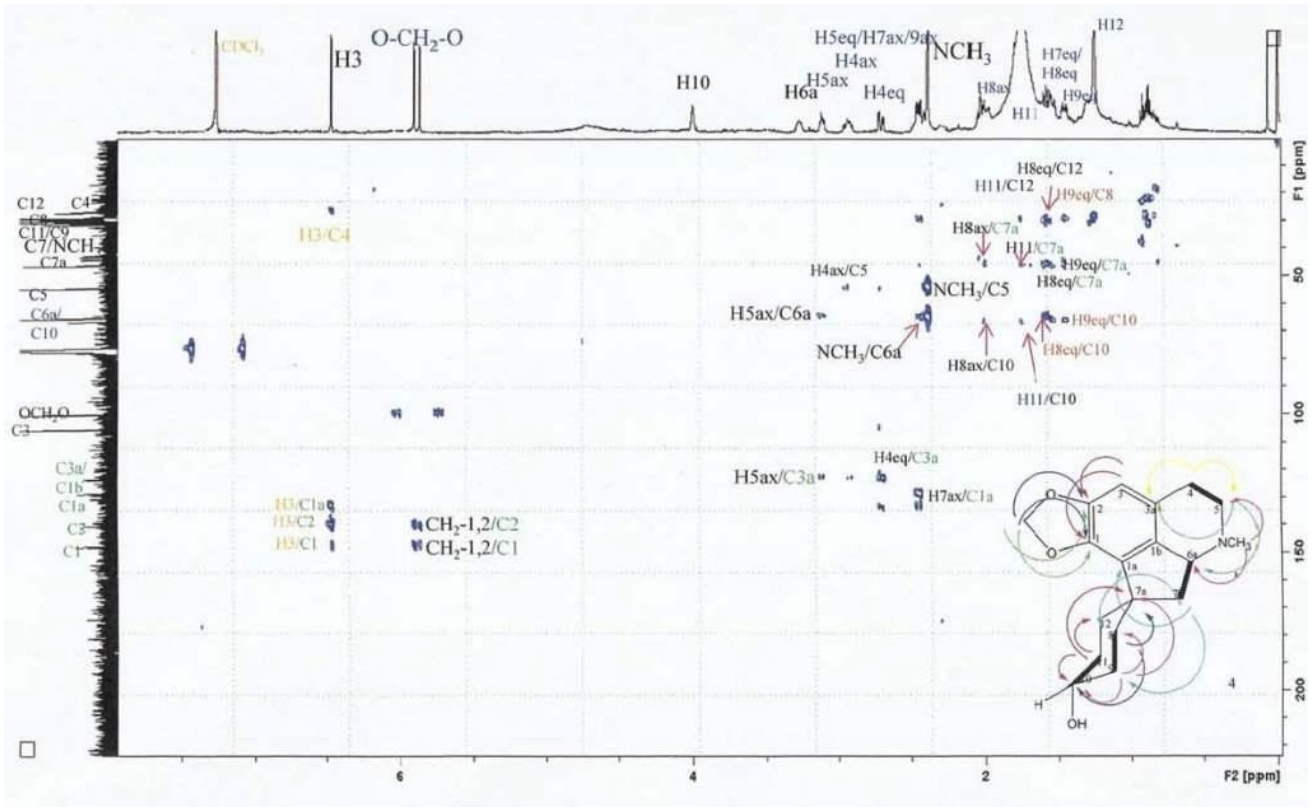
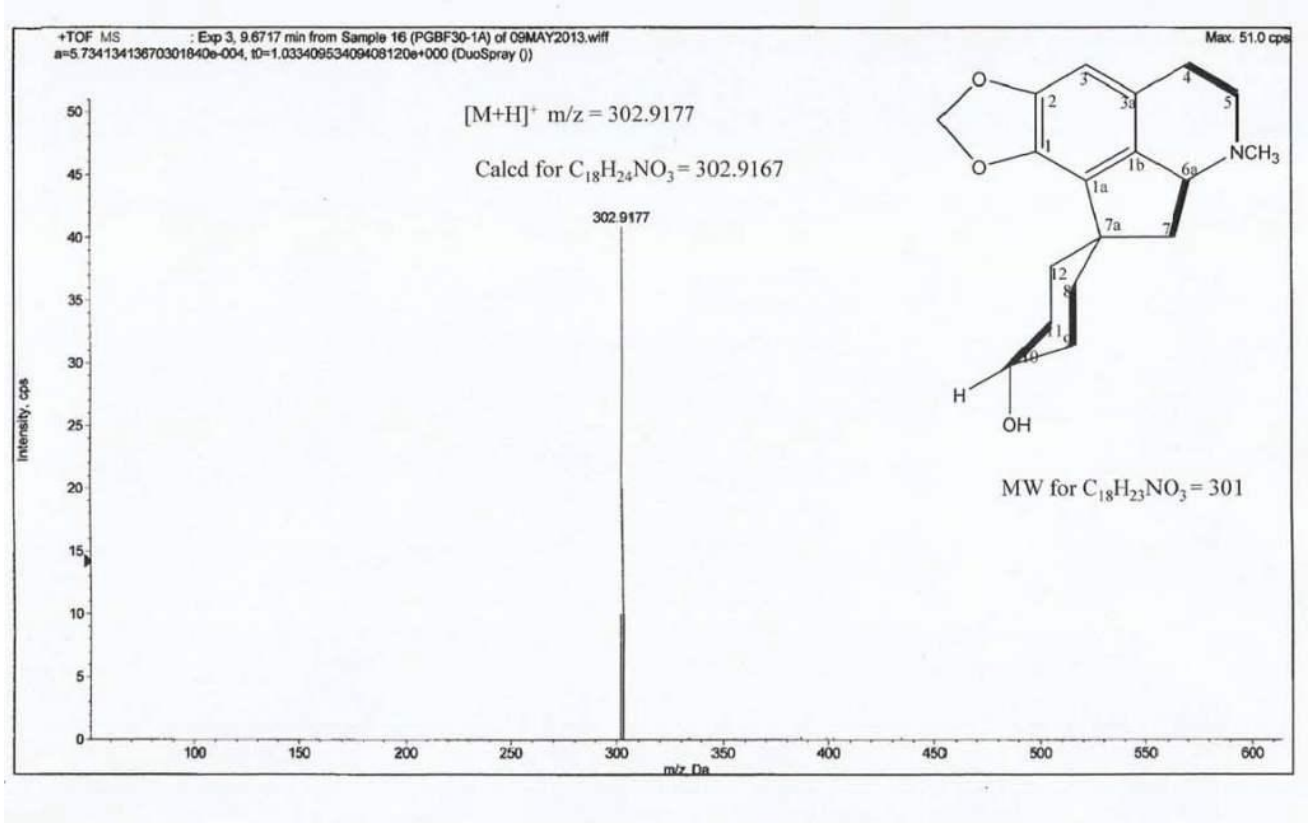


Figure S25. LCMS Triple TOF-MS spectrum of hexahydromecambrine A (**4**).



Hexahydromecambrine A (**4**)**:** $C_{18}H_{23}NO_3$, amorphous solid. $[\alpha]_D^{29}$ = +100 (c=0.00003, $CHCl_3$). LCMS-Triple-TOF *m/z*: 302.9177 $[M+H]^+$ (calcd for $C_{18}H_{24}NO_3$, 302.9167). ^{1}H NMR (600 MHz, CD_3OD, δ, ppm, *J*/Hz): 6.46 (1H, s, H-3), 2.93 (1H, m, H-4ax), 2.71 (1H, m, H-4eq), 3.11 (1H, m, H-5ax), 2.46 (1H, m, H-5eq), 3.26 (1H, m, H-6a), 2.44 (1H, m, H-7ax), 1.58 (1H, m, H-7eq), 2.03 (1H, m, H-8ax), 1.54 (1H, m, H-8eq), 2.41 (1H, m, H-9ax), 1.46 (1H, m, H-9eq), 4.00 (1H, br, m H-10ax), 1.75 (2H, m, H-11), 1.25 (2H, m, H-12), 2.39 (3H, s, NCH_3), 5.90 (1H, d, *J*=1.2, O-CH_2-O), 5.86 (1H, d, *J*=1.2, O-CH_2-O). ^{13}C NMR (150 MHz, CD_3OD, δ, ppm): 148.1 (C-1), 129.0 (C-1a), 131.0 (C-1b), 140.8 (C-2), 105.9 (C-3), 124.0 (C-3a), 27.3 (C-4), 54.9 (C-5), 65.7 (C-6a), 44.3 (C-7), 46.6 (C-7a), 30.2 (C-8), 31.7 (C-9), 67.1 (C-10), 31.0 (C-11), 29.7 (C-12), 43.2 (NCH_3), 100.5 (O-CH_2-O).