Supplementary Information

Identification of Alkaloids from *Hippeastrum aulicum* (Ker Gawl.) Herb. (Amaryllidaceae) Using CGC-MS and Ambient Ionization Mass Spectrometry (PS-MS and LS-MS)

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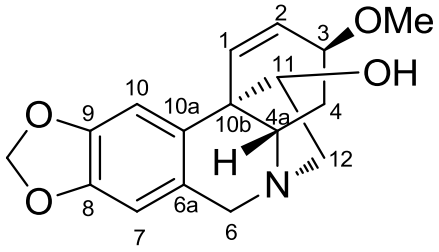

Figure S1. Structure of haemanthamine (**16**).

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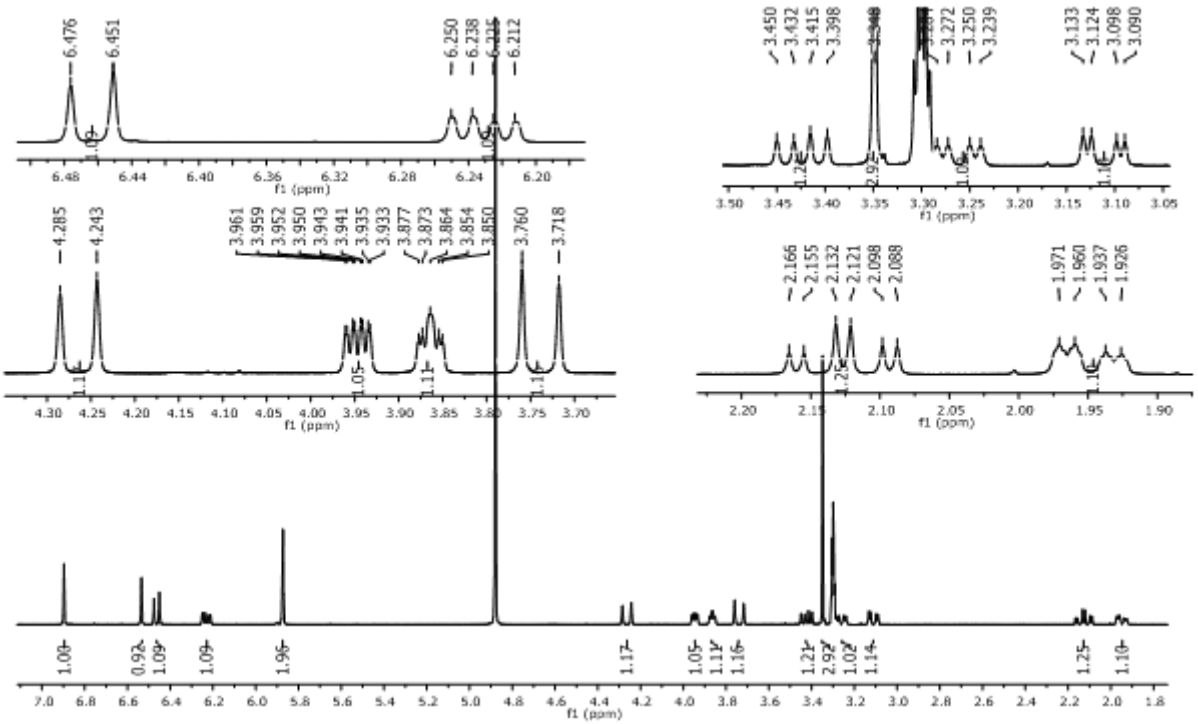

Figure S2. ^{1}H NMR spectrum (400 MHz, CD_3OD) of haemanthamine (**16**).

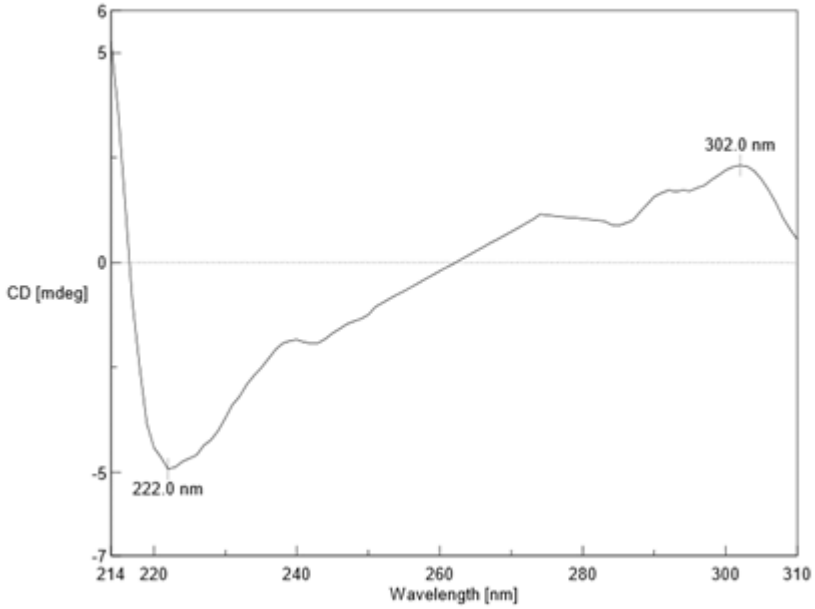

Figure S3. Circular dichroism spectrum of haemanthamine (**16**).

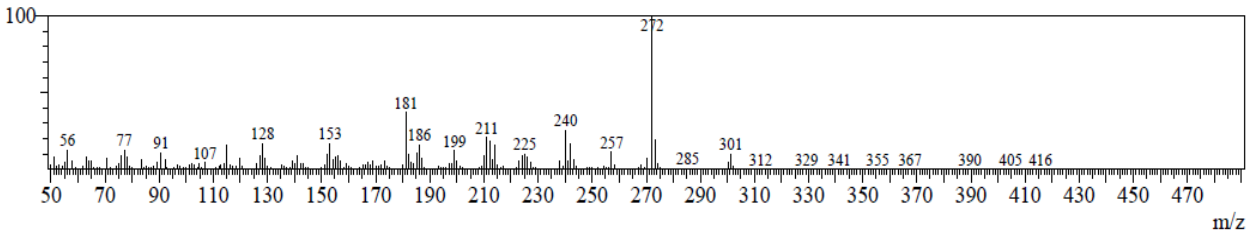

Figure S4. EI-MS spectrum of haemanthamine (**16**).

Table S1. [1]H NMR (400 MHz, CD_3OD) data of haemanthamine (**16**) compared with the literature (360 MHz, $CDCl_3$/1%C_5D_5N)[1]

Position	δ_H (*J* in Hz) Compound **16**	δ_H (*J* in Hz) literature
1	6.46 d (10.0)	6.36 d (10.0)
2	6.23 dd (10.0, 5.2)	6.25 dd (10.0, 5.0)
3	3.86 m	3.82 m
4a	3.26 dd (13.2, 4.8)	3.25 dd (13.6, 4.6)
4α	2.13 td (13.6, 13.6, 3.6)	2.11 ddd (13.7, 13.6, 4.2)
4β	1.95 dd (13.6, 4.4)	1.96 ddd (13.7, 4.6, < 1)
6α	3.74 d (16.8)	3.72 d (16.8)
6β	4.26 d (16.8)	4.25 d (16.8)
7	6.53 s	6.41 s
10	6.89 s	6.74 s
11	3.95 ddd (7.2, 3.6, 0.8)	3.96 dd (6.7, 3.3)
12*endo*	3.43 dd (14.0, 6.8)	3.30 dd (13.9, 6.7)
12*exo*	3.11dd (13.6, 3.6)	3.19 dd (13.9, 3.3)
OCH_2O	5.87 br s	5.81 (2d) (1.3)
3-OMe	3.34 s	3.36 s

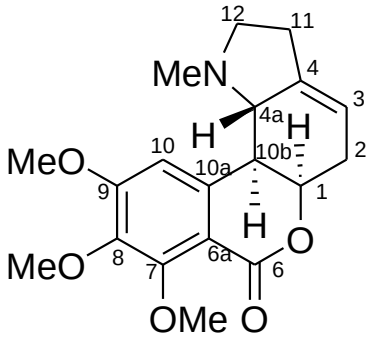

Figure S5. Structure of albomaculine (**29**).

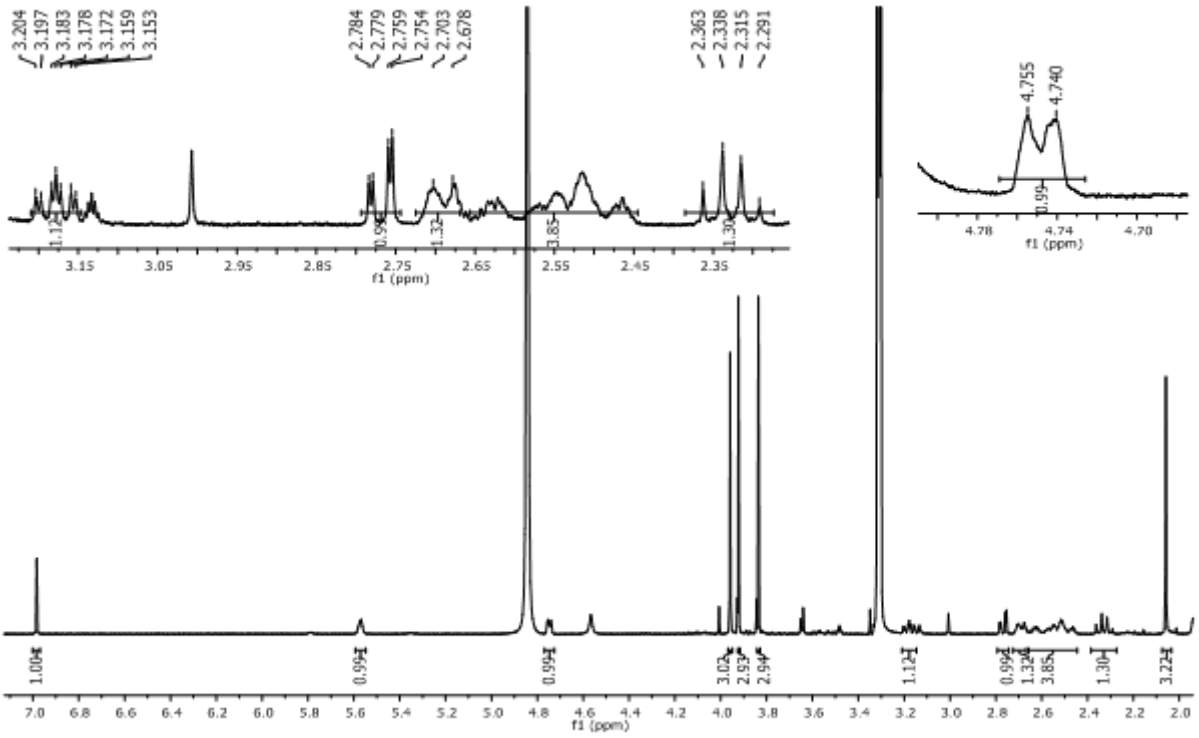

Figure S6. ^{1}H NMR spectrum (400 MHz, CD_3OD) of albomaculine (**29**).

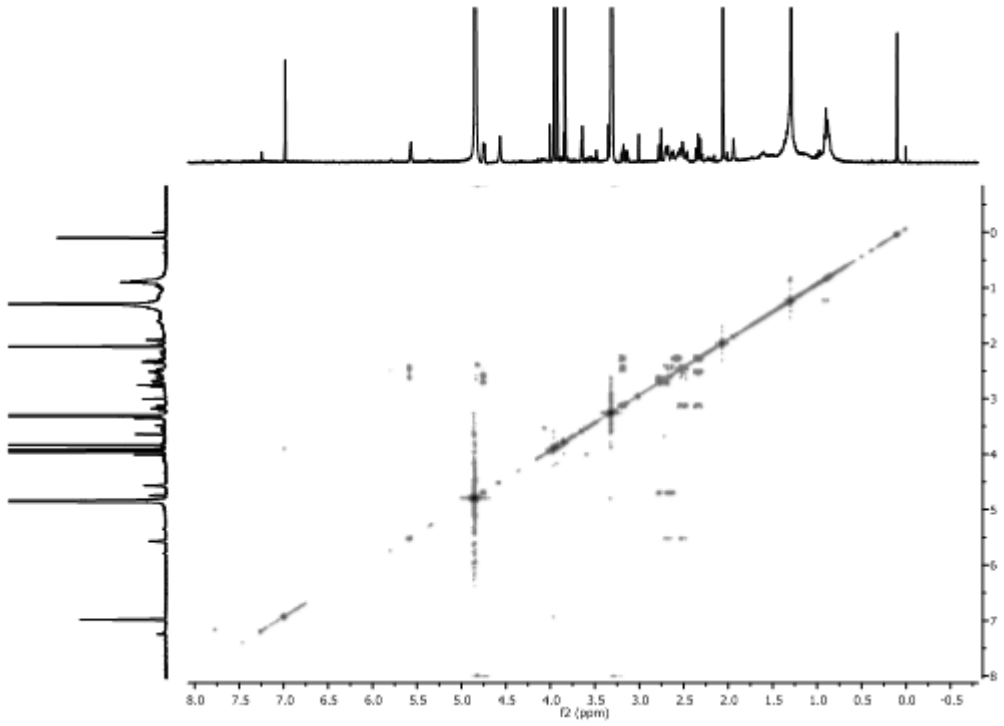

Figure S7. ^{1}H-^{1}H correlation spectroscopy (COSY) spectrum (400 MHz, CD_3OD) of albomaculine (**29**).

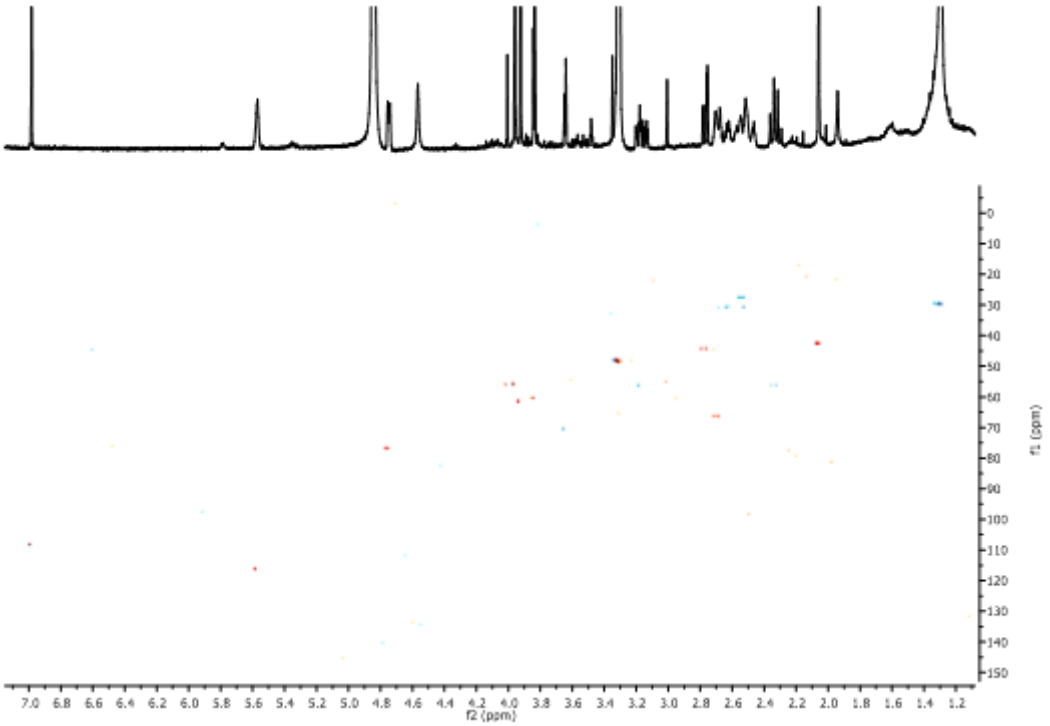

Figure S8. Heteronuclear single-quantum correlation (HSQC) spectrum (400 MHz, CD_3OD) of albomaculine (**29**).

Table S2. ^1H NMR and COSY (CD_3OD, 400 MHz) data of albomaculine (**29**) compared with the literature (400 MHz, $CDCl_3$)[2]

Position	δ_H (*J* in Hz) Compound **29**	COSY	δ_H (*J* in Hz) literature
1	4.75 br d (6.0)	H-2α, H-2β	4.68 br m
2α	2.43-2.63 br m	H-1	2.55-2.60 br m
2β	2.43-2.63 br m	H-1	2.55-2.60 br m
3	5.59-5.55 br m	H-2α, H-2β	5.48 br m
4a	2.68 br d (10.0)	H-10b	2.72 d (10.0)
10	6.98 s	9-OMe	6.78 s
10b	2.76 dd (10.0, 2.0)	H-4a	2.63 d (10.0)
11α	2.43-2.63 br m	H-12α, H-12β	2.45-2.53 br m
11β	2.43-2.63 br m	H-12α, H-12β	2.45-2.53 br m
12α	3.17 ddd (10.0, 7.6, 2.4)	H-11α, H-11β, H-12β	3.13 ddd (9.6, 7.2, 3.6)
12β	2.32 q (10.0)	H-11α, H-11β, H-12α	2.23 q (9.6)
7-OMe	3.95 s		3.99 s
8-OMe	3.83 s		3.89 s
9-OMe	3.92 s	H-10	3.91s
N-Me	2.05 s		2.05 s

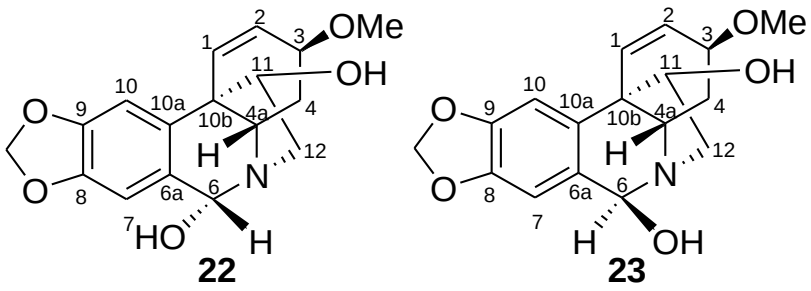

Figure S9. Structure of haemanthidine (**22**) and 6-epihaemanthidine (**23**).

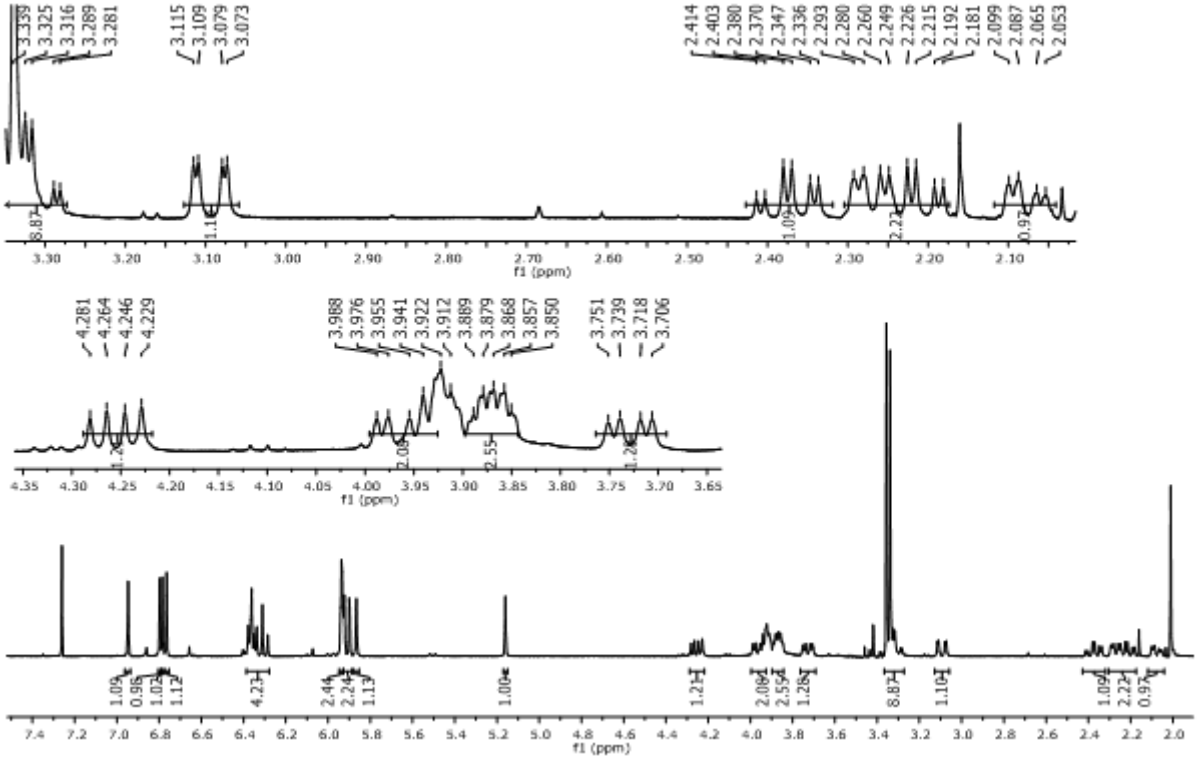

Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of haemanthidine (**22**) and 6-epihaemanthidine (**23**).

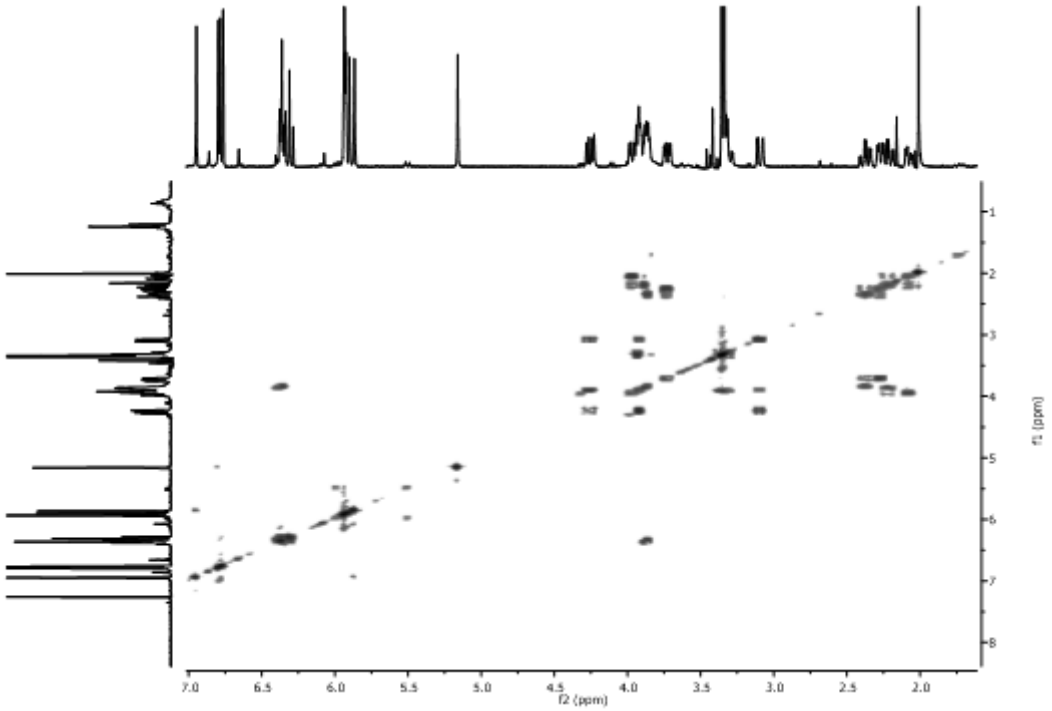

Figure S11. ^{1}H-^{1}H correlation spectroscopy (COSY) spectrum (400 MHz, $CDCl_3$) of haemanthidine (**22**) and 6-epihaemanthidine (**23**).

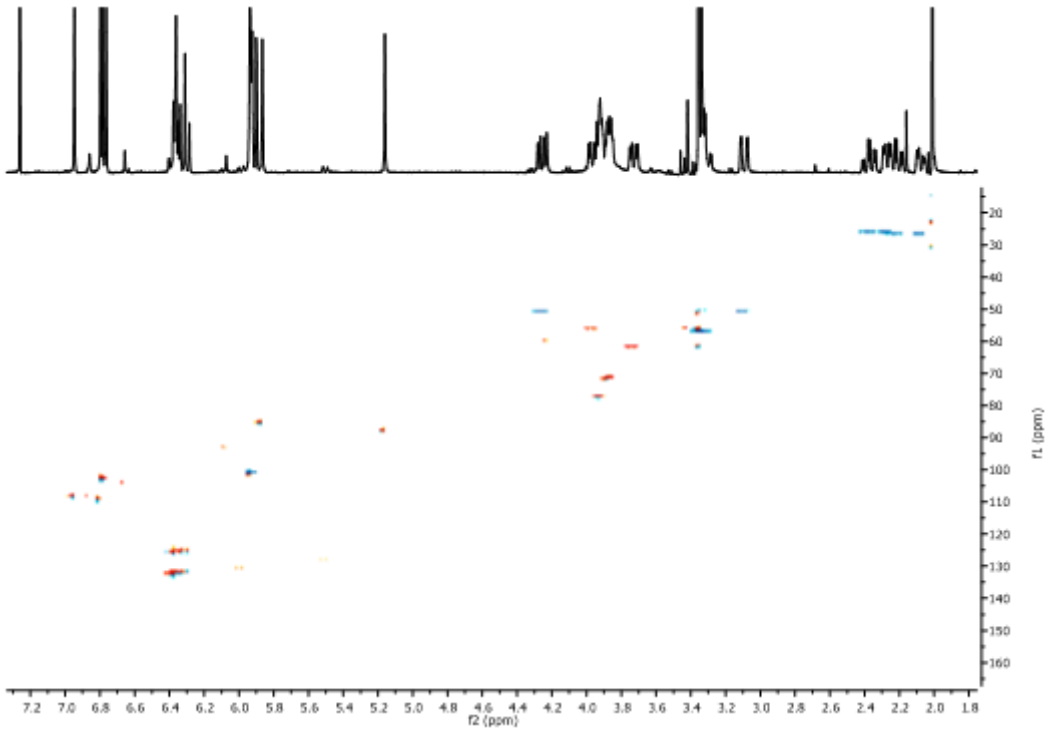

Figure S12. Heteronuclear single-quantum correlation (HSQC) spectrum (400 MHz, $CDCl_3$) of haemanthidine (**22**) and 6-epihaemanthidine (**23**).

Table S3. ^{1}H NMR (400 MHz, $CDCl_3$) data of compounds **22** e **23** compared with the literature (360 MHz, $CDCl_3$/1%C_5D_5N)[1]

Position	δ_H (*J* in Hz) Compounds **22 / 23**	δ_H (*J* in Hz) literature
1	6.28-6.38 m	6.33 d (10.1)
2	6.28-6.38 m	6.27 dd (10.1, 4.8)
3	3.87 m	3.85 m
4α	2.38 ddd (13.6, 13.6, 4.4) / 2.27 br dd (12.4, 4.8)	2.36 ddd (13.5, 13.5, 4.3) / 2.21 ddd (13.7, 13.7, 4.3)
4β	2.20 dd (13.6, 4.4) / 2.07 dd (13.6, 4.8)	2.12 ddd (13.5, 4.3, 1.0) / 2.0 ddd (13.7, 4.5, 1.0)
4a	3.73 dd (13.2, 4.8) / 3.28-3.36 m	3.56 dd (13.5, 4.3) / 3.20 m
6α	– / 5.16 s	– / 5.02 s
6β	5.87 s / –	5.69 s / –
7	6.95 s / 6.80 s	6.94 s / 6.79 s
10	6.76 s / 6.78 s	6.70 s / 6.73 s
11 *endo*	3.96 m	3.92 m
12 *endo*	4.26 dd (14.0, 6.8) / 3.28-3.36 m	4.20 dd (14.1, 6.9) / 3.30 m
12 *exo*	3.09 dd (14.4, 2.4) / 3.28-3.36 m	2.96 dd (14.1, 2.7) / 3.20 m
OCH_2O	5.91 2d (1.6) / 5.93 2d (1.3)	5.83 2d (1.3) / 5.86 2d (1.3)
OMe	3.36 s / 3.34 s	3.32 s / 3.28 s

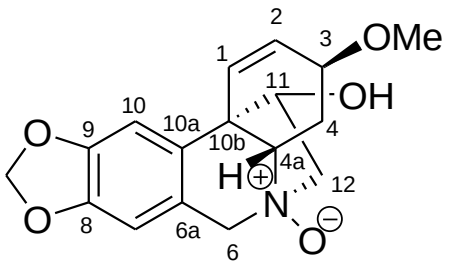

Figure S13. Structure of haemanthamine *N*-oxide (**1**).

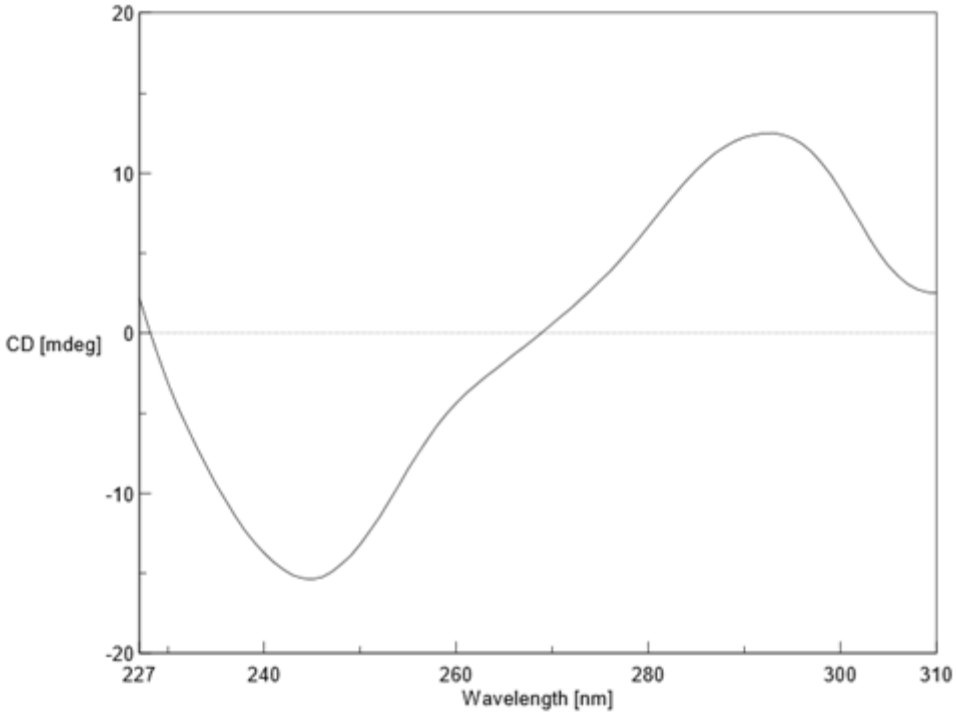

Figure S14. Circular dichroism spectrum of haemanthamine *N*- oxide (**1**).

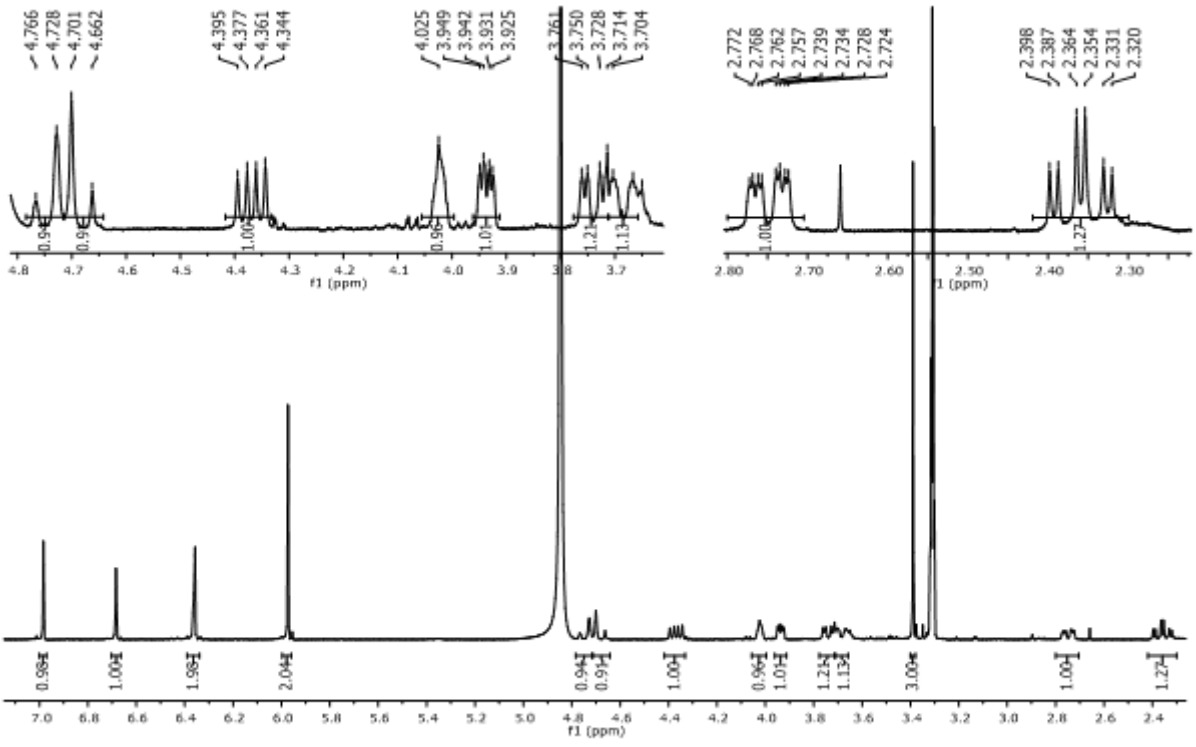

Figure S15. ^{1}H NMR spectrum (400 MHz, CD_3OD) of haemanthamine *N*-oxide (**1**).

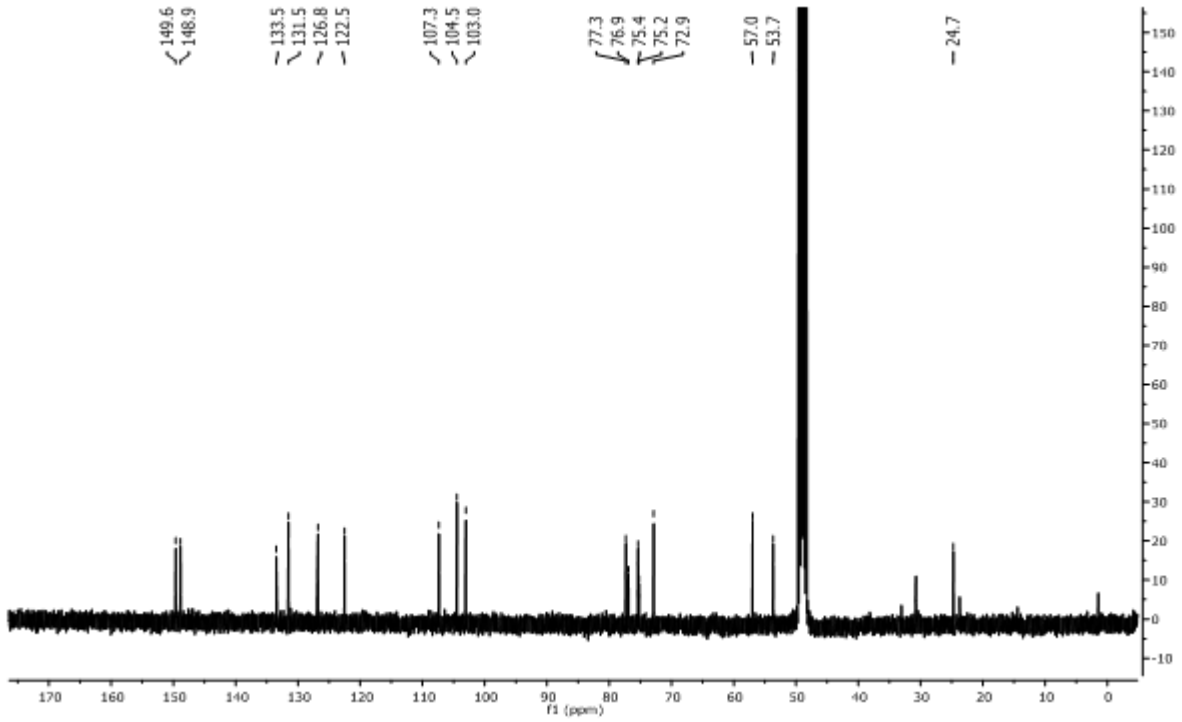

Figure S16. ^{13}C NMR spectrum (100 MHz, CD_3OD) of haemanthamine *N*-oxide (**1**).

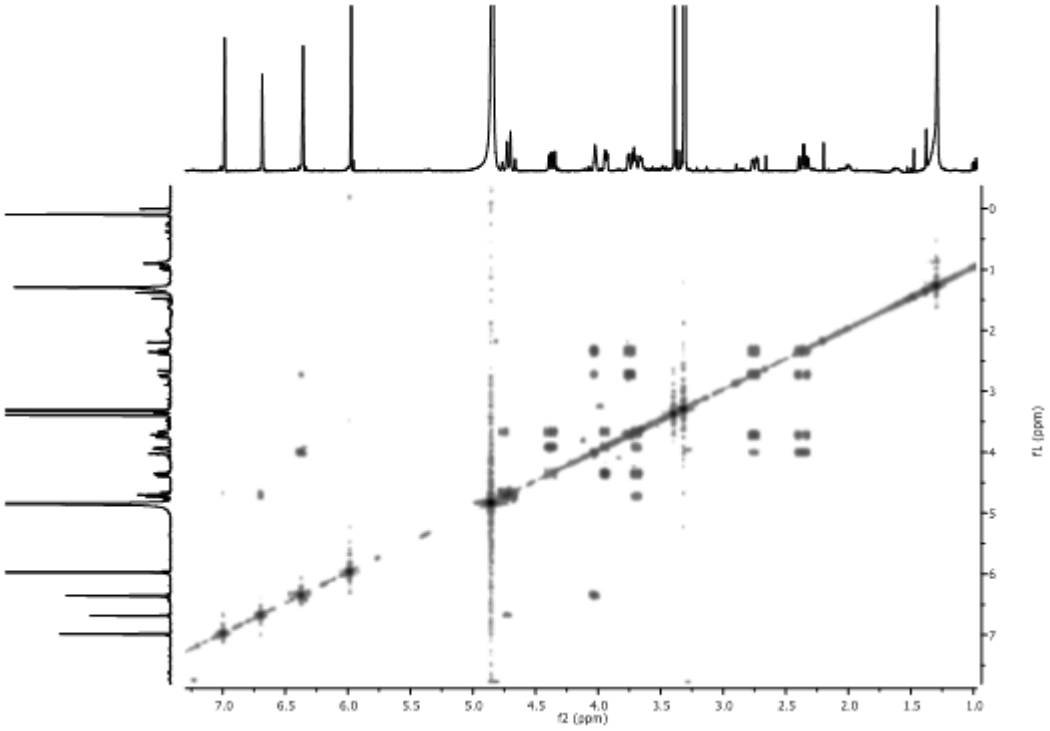

Figure S17. ^{1}H-^{1}H correlation spectroscopy (COSY) spectrum (400 MHz, CD_3OD) of haemanthamine *N*- oxide (**1**).

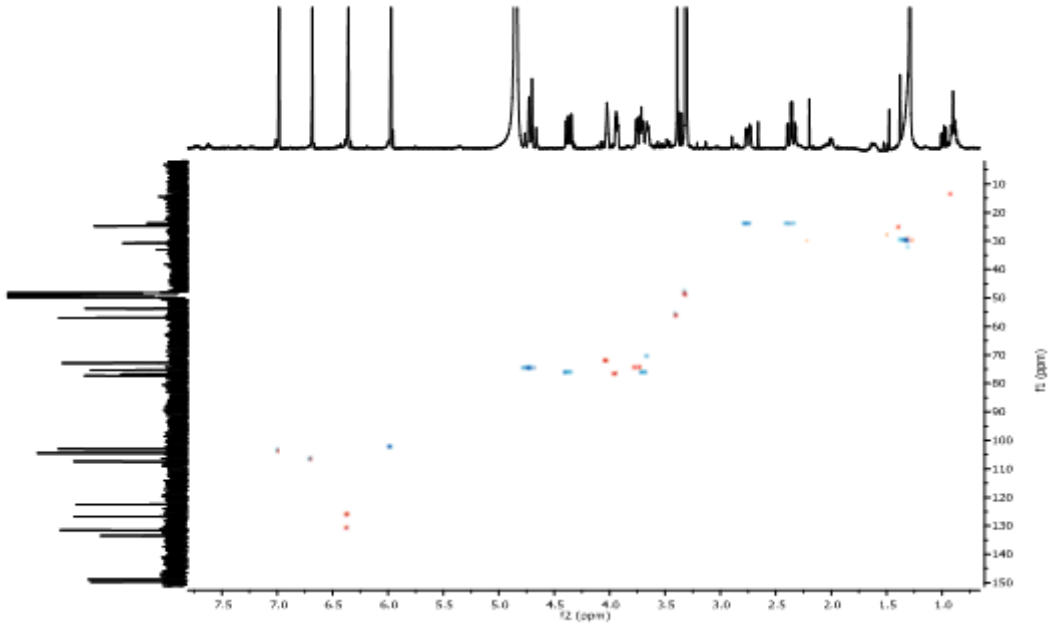

Figure S18. Heteronuclear single-quantum correlation (HSQC) spectrum (400 MHz, CD_3OD) of haemanthamine *N*-oxide (**1**).

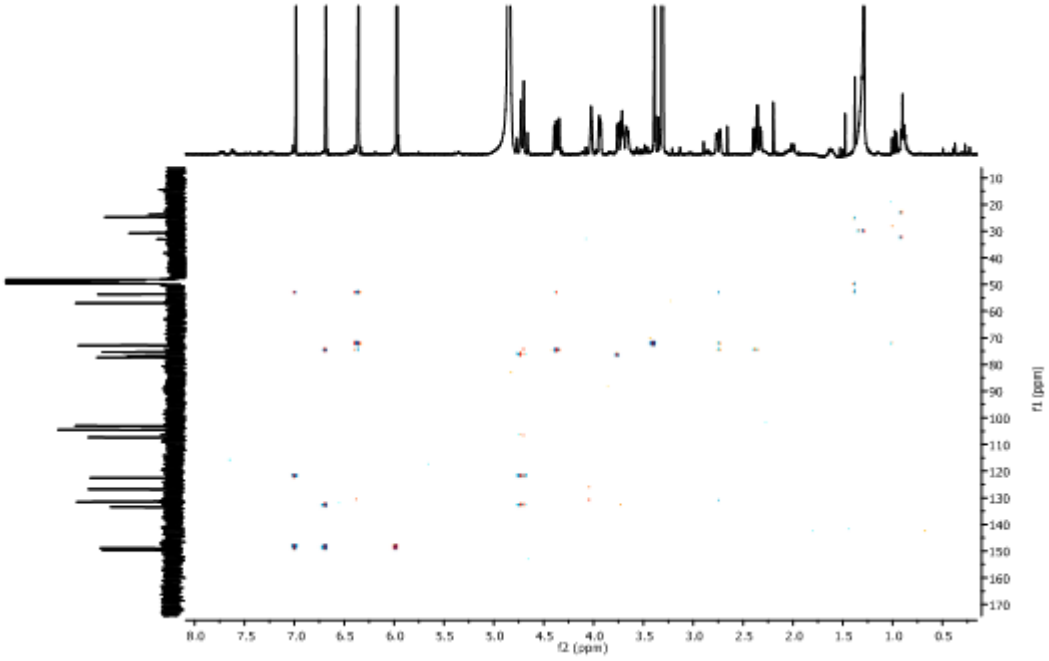

Figure S19. Heteronuclear multiple bond correlation (HMBC) spectrum (400 MHz, CD_3OD) of haemanthamine *N*-oxide (**1**).

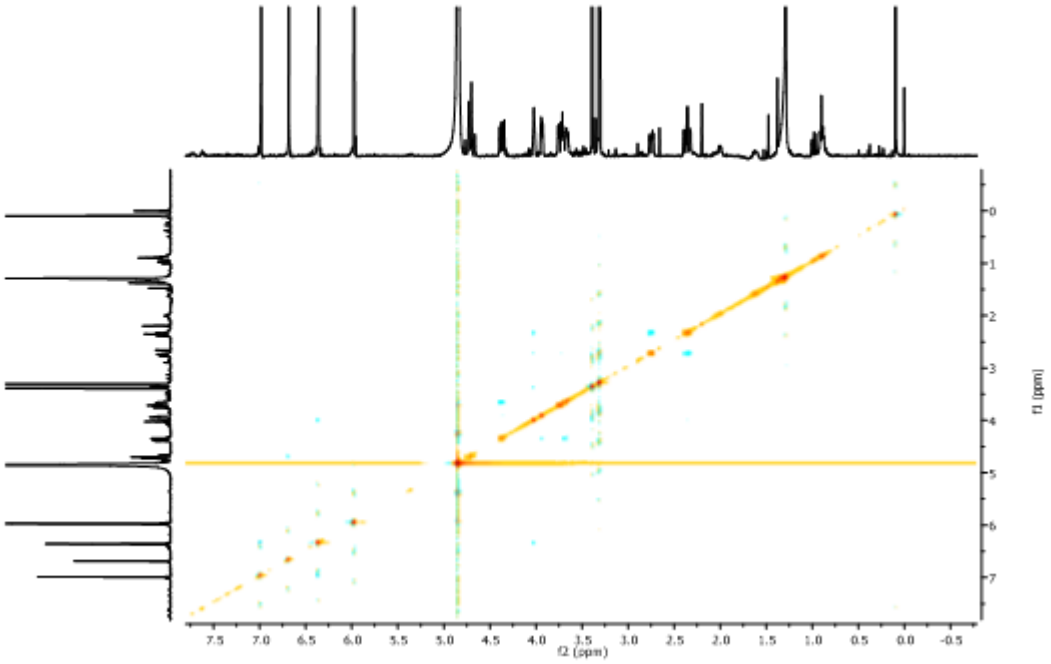

Figure S20. ^{1}H-^{1}H correlation spectroscopy (NOESY) spectrum (400 MHz, CD_3OD) of haemanthamine *N*-oxide (**1**).

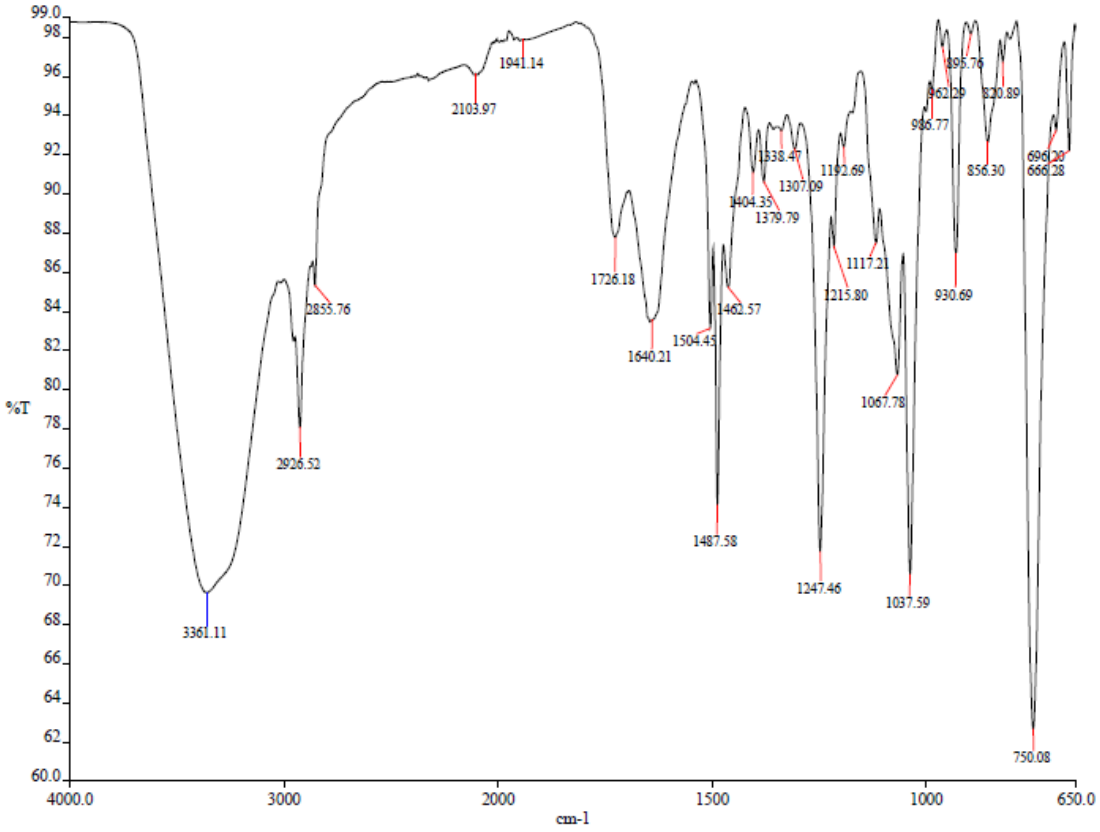

Figure S21. IR spectrum of haemanthamine *N*-oxide (**1**).

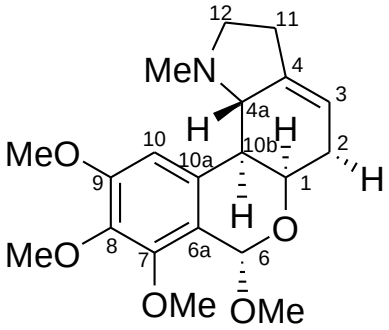

Figure S22. Structure of 7-methoxy-*O*-methyllycorenine (**12**).

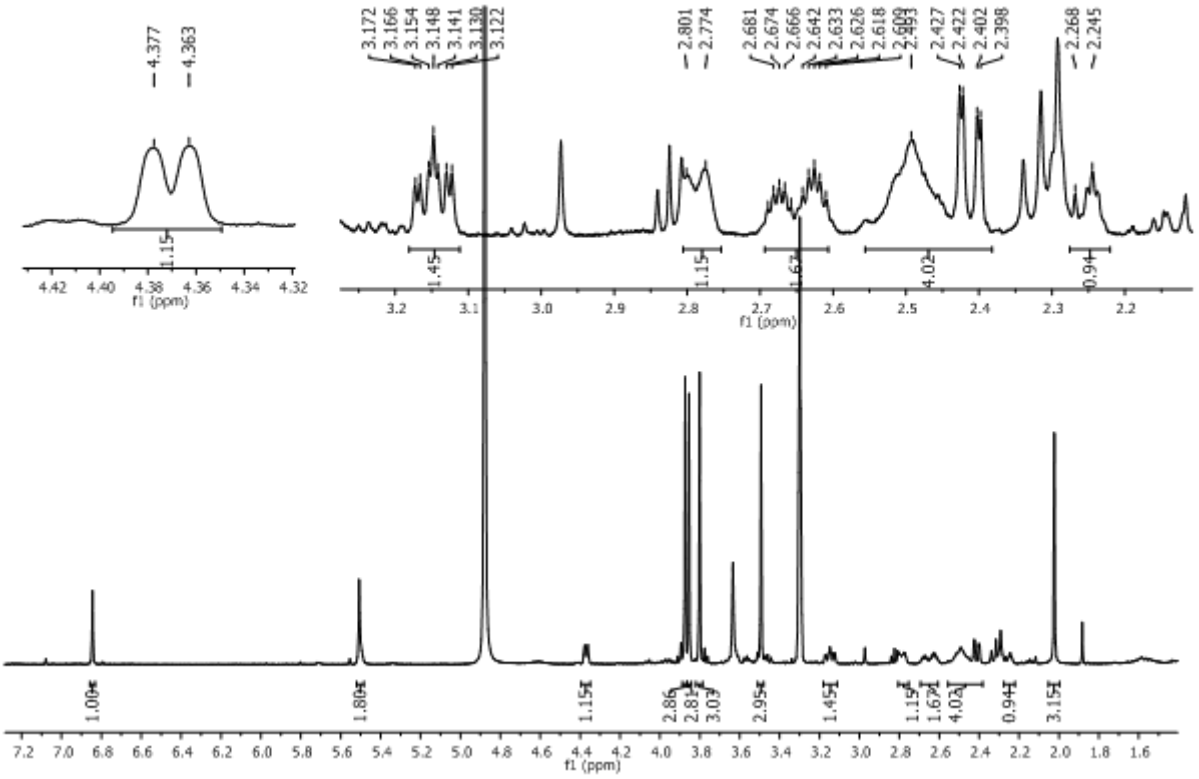

Figure S23. ^{1}H NMR spectrum (400 MHz, CD_3OD) of 7-methoxy-*O*-methyllycorenine (**12**).

Table S4. ^{1}H NMR (400 MHz, CD_3OD) data of 7-methoxy-*O*-methyllycorenine (**12**) compared with the literature (500 MHz, CD_3OD)[2]

Position	δ_H (*J* in Hz) Compound **12**	δ_H (*J* in Hz) literature
1	4.37 d (5.6)	4.40 br d (6.5)
2α	2.65 m	2.67 ddt (19.0, 6.5, 3.0)
2β	2.26 m	2.29 dt (19.5, 3.0)
3	5.51 br s	5.55 br s
4a	2.79 br d (9.6)	2.92 br d (10.0)
6	5.51 br s	5.52 s
10	6.84 s	6.85 s
10b	2.41 dd (9.6, 2.0)	2.47 dd (10.0, 2.0)
11α	2.44-2.55 m	2.49-2.58 m
11β	2.44-2.55 m	2.49-2.58 m
12α	3.15 ddd (10.0, 7.2, 2.8)	3.22 ddd (10.5, 7.5, 3.0)
12β	2.44-2.55 m	2.42 m
6-OMe	3.49 s	3.51 s
7-OMe	3.87 s	3.89 s
8-OMe	3.80 s	3.82 s
9-OMe	3.85 s	3.87 s
N-Me	2.02 s	2.11 s

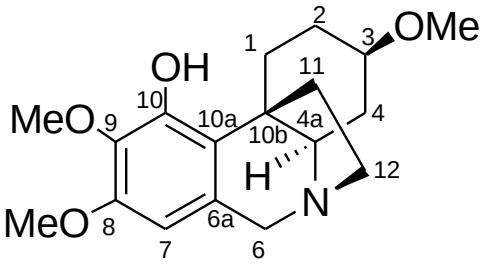

Figure S24. Structure of aulicine (**15**).

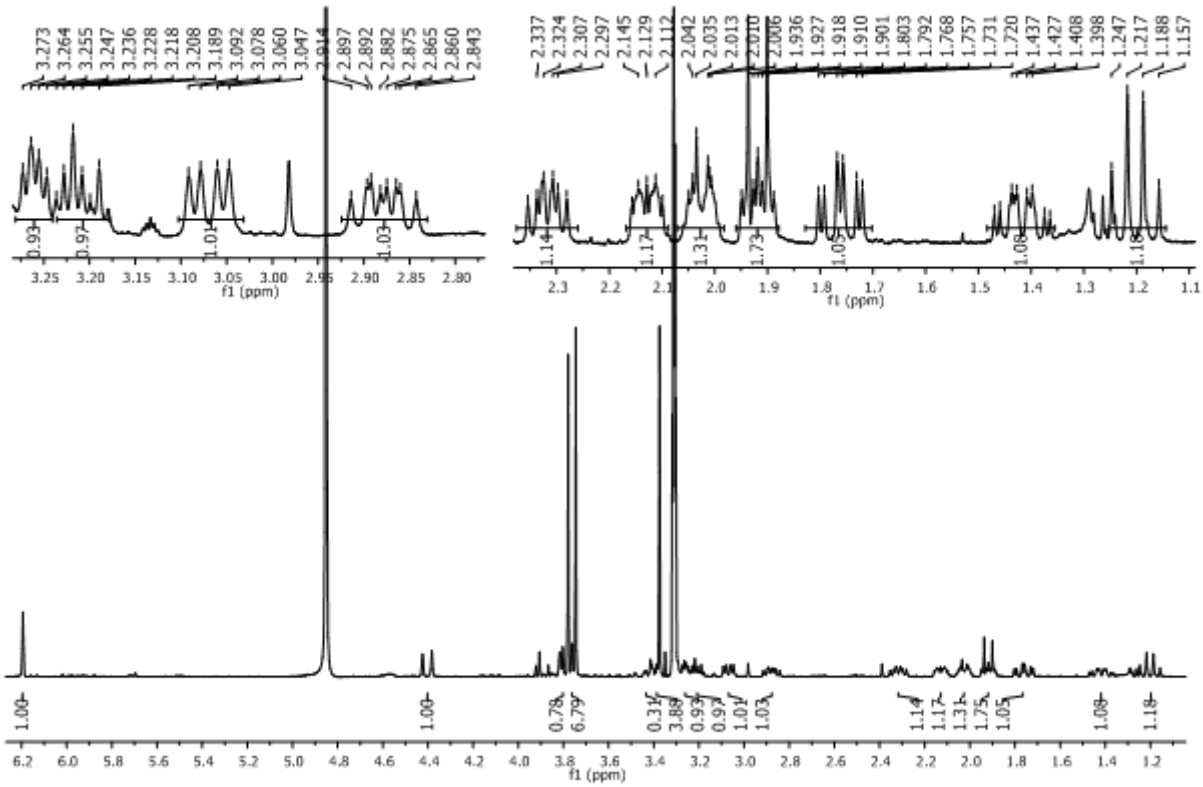

Figure S25. ^{1}H NMR spectrum (400 MHz, CD_3OD) of aulicine (**15**).

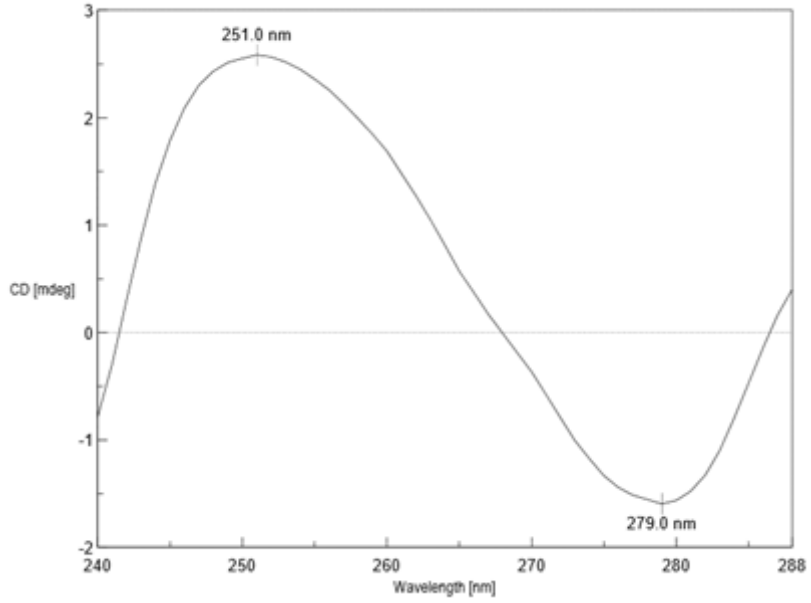

Figure S26. Circular dichroism spectrum of aulicine (**15**).

Table S5. ^{1}H NMR (400 MHz, CD_3OD) data of aulicine (**15**) compared with the literature (400 MHz, $CDCl_3$)[2]

Position	δ_H (*J* in Hz) compound **15**	δ_H (*J* in Hz) literature
1α	1.76 td (14.0, 4.4)	1.77 td (14.0, 4.0)
1β	3.23 m	3.10-3.20 m
2α	2.04 m	2.04 m
2β	1.42 tdd (13.2, 11.6, 4.0)	1.44 tdd (13.5, 11.5, 4.0)
3	3.23 m	3.10-3.20 m
4α	2.13 br d (13.2)	2.13 br d (12.4)
4β	1.20 q (12.0)	1.21 q (12.4)
4a	3.07 dd (12.4, 5.6)	2.93 dd (12.4, 5.2)
6α	4.40 d (16.4)	4.38 d (16.8)
6β	3.78 d (16.8)	3.71 d (16.8)
7	6.19 s	6.10 s
11*endo*	1.92 ddd (12.4, 8.8, 3.6)	1.90 ddd (12.0, 8.8, 3.2)
11*exo*	2.31 ddd (12.0, 10.8, 6.8)	2.23 ddd (12.4, 10.4, 6.4)
12*endo*	2.88 ddd (12.8, 8.8, 6.8)	2.78 ddd (12.8, 8.8, 6.4)
12*exo*	3.40 ddd (12.8, 10.0, 3.2)	3.36 ddd (12.8, 10.0, 3.2)
3-OMe	3.37 s	3.38 s
8-OMe	3.74 s	3.80 s
9-OMe	3.78 s	3.87 s

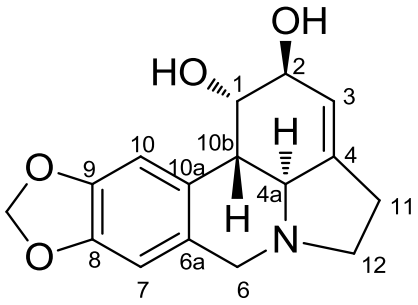

Figure S27. Structure of lycorine (**25**).

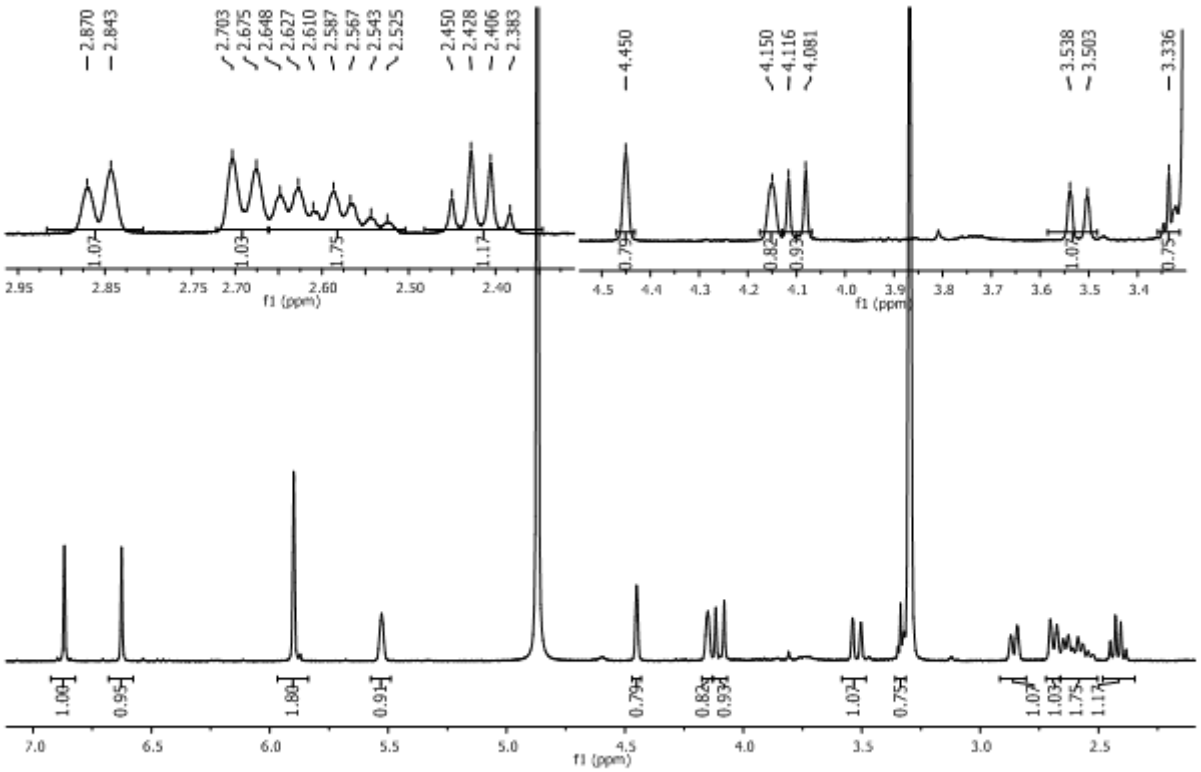

Figure S28. ^{1}H NMR spectrum (400 MHz, CD_3OD) of lycorine (**25**).

Table S6. ^{1}H NMR (400 MHz, CD_3OD) data of lycorine (**25**) compared with the literature (300 MHz, DMSO-d_6)[3]

Position	δ_H (J in Hz) Compound **25**	δ_H (J in Hz) literature
1	4.45 s	4.27 br s
2	4.15 s	3.97 br s
3	5.52 s	5.37 br s
4a	2.86 d (10.8)	2.60 d (10.6)
6α	3.52 d (14.0)	3.32 d (14.4)
6β	4.10 d (14.0)	4.02 d (14.4)
7	6.62 s	6.68 s
10	6.87 s	6.81 s
10b	2.68 d (11.2)	2.50 m
11α	2.58 m	2.44 m
11β	2.58 m	2.44 m
12α	2.41 q (8.8)	2.19 ddd (14.4, 8.6, 1.5)
12β	3.33 m	3.19 dd (14.4, 7.5)
OCH_2O	5.89 s	5.94 s ; 5.96 s

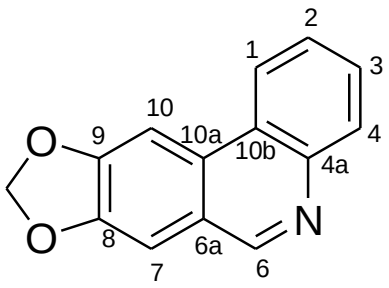

Figure S29. Structure of trisphaeridine (**3**).

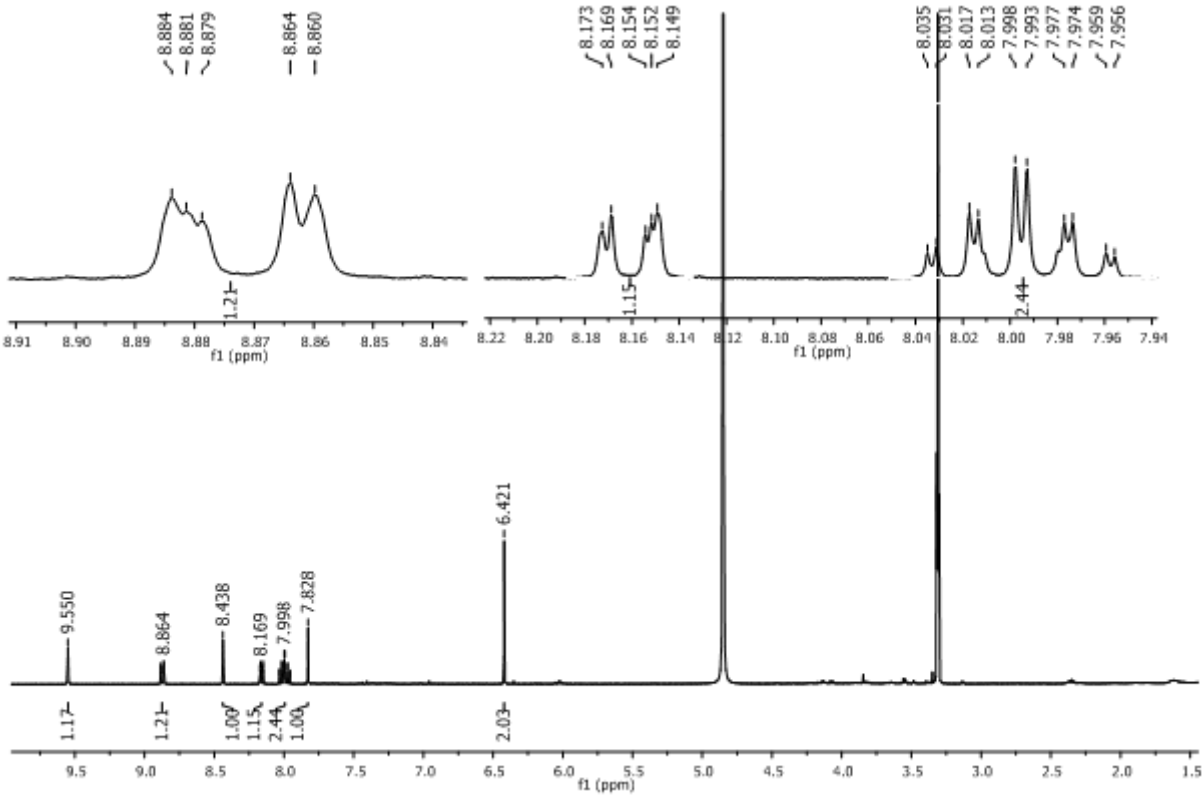

Figure S30. ^{1}H NMR spectrum (400 MHz, CD_3OD) of trisphaeridine (**3**).

Table S7. ^{1}H NMR (400 MHz, CD_3OD) data of trisphaeridine (**3**) compared with the literature (200 MHz, $CDCl_3$)[4]

Position	δ_H (*J* in Hz) Compound **3**	δ_H (*J* in Hz) literature
1	8.86 dd (8.0, 2.0)	8.36 dddd (8.0, 1.8, 1.0, 1.0)
2	7.97 td (7.6, 1.6)	7.61ddd (8.0, 7.0, 1.7)
3	8.01 td (7.6, 1.6)	7.67 ddd (7.0, 7.0, 1.8)
4	8.17 dd (8.0, 1.6)	8.11 ddd (7.0, 1.7, 1.0)
6	9.55 s	9.06 s
7	7.83 s	7.32 s
10	8.44 s	7.89 s
OCH_2O	6.42s	6.15 s

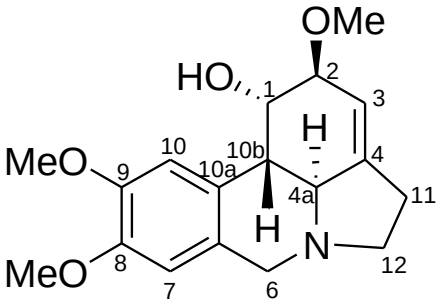

Figure S31. Structure of galanthine (**21**).

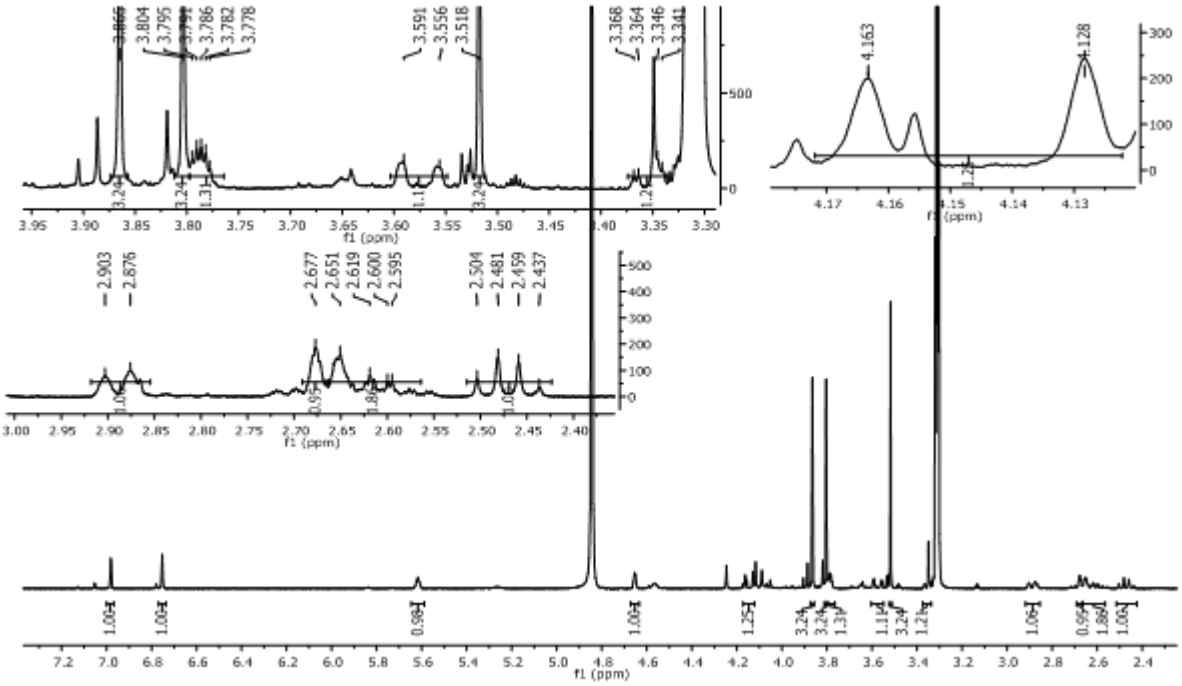

Figure S32. ^{1}H NMR spectrum (400 MHz, CD_3OD) of galanthine (**21**).

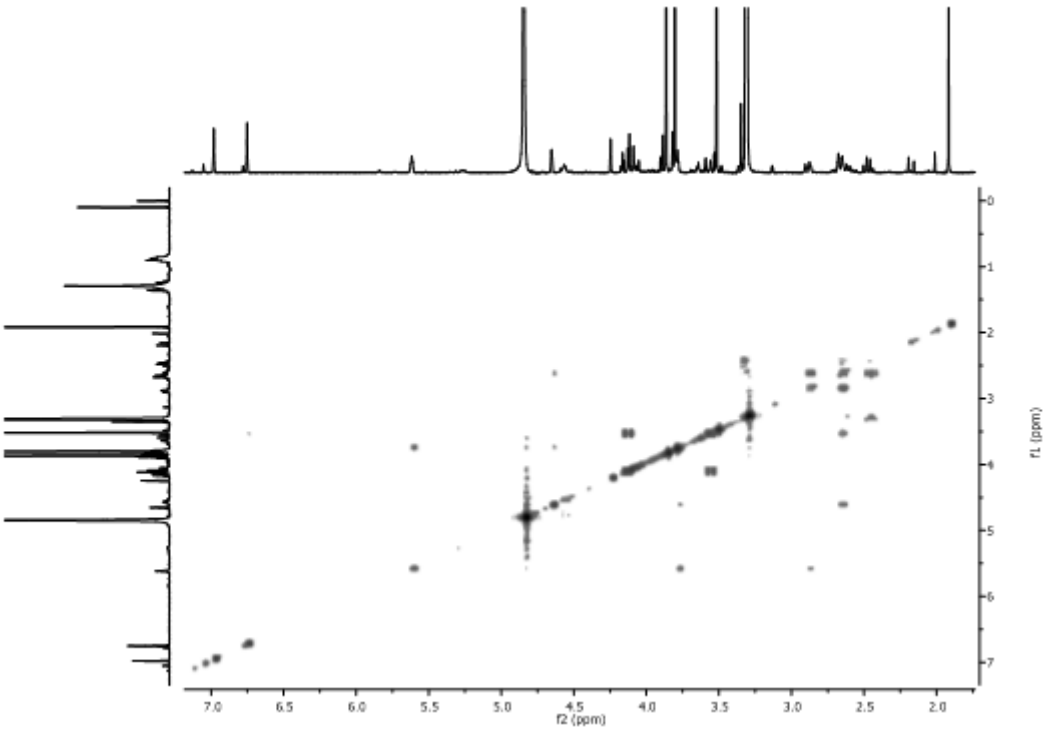

Figure S33. ^{1}H-^{1}H correlation spectroscopy (COSY) spectrum (400 MHz, CD_3OD) of galanthine (**21**).

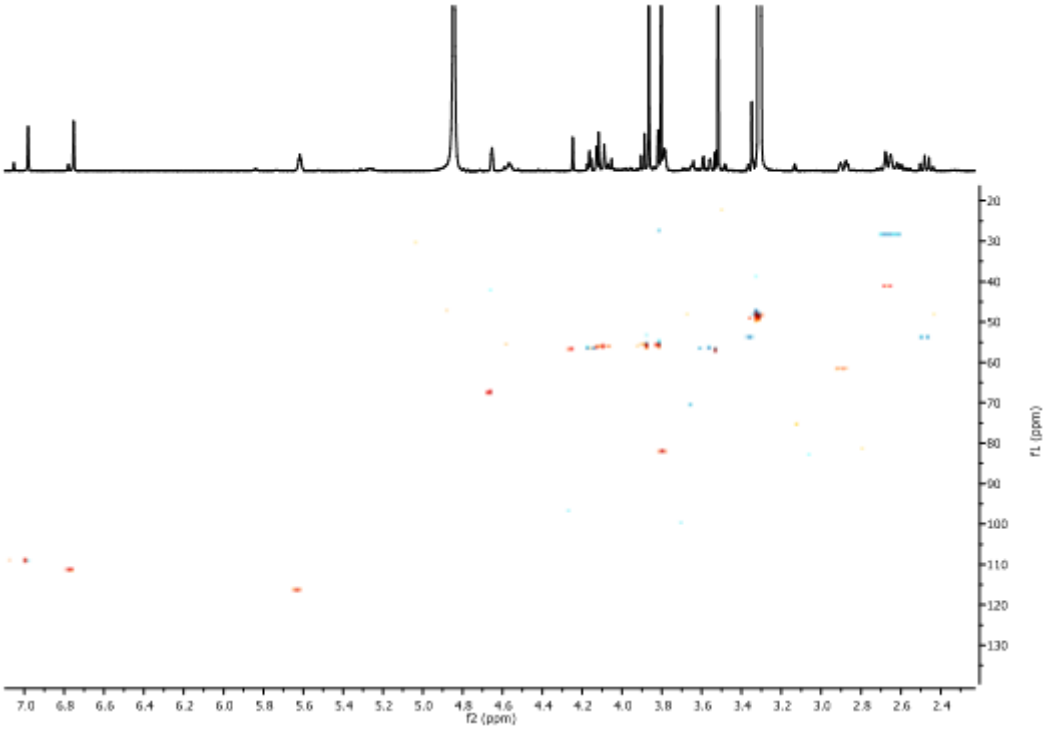

Figure S34. Heteronuclear single-quantum correlation (HSQC) spectrum (400 MHz, CD_3OD) of galanthine (**21**).

Table S8. [1]H NMR (400 MHz, CD_3OD) data of galanthine (**21**) compared with the literature (200 MHz, $CDCl_3$)[5]

Position	δ_H (*J* in Hz) Compound **21**	COSY	δ_H (*J* in Hz) literature
1	4.65 br s	H-2, H-10b	4.55 s
2	3.78 m	H-1, H-3	3.72 m
3	5.62 br s	H-2, H-4a	5.55 br s
4a	2.89 d (10.8)	H-3, H-10b	2.65 s
6α	3.57 br d (14.0)	H-6β	3.40 br d (14.0)
6β	4.14 br d (14.0)	H-6α	4.05 d (14.0)
7	6.75 s		6.52 s
10	6.98 s		6.78 s
10b	2.68 br s	H-1, H-4a	2.65 s
11α	2.56-2.66 m	H-12α, H-12β	2.45-2.60 m
11β	2.56-2.66 m	H-12α, H-12β	2.45-2.60 m
12α	2.47 q (8.8)	H-11α, H-11β, H-12β	2.25 dd (16.4, 8.2)
12β	3.35 br dd (8.8, 2.0)	H-11α, H-11β, H-12α	3.25 ddd (16.4, 10.0, 6.0)
9-OMe	3.86 s		3.78 s
8-OMe	3.80 s		3.74 s
2-OMe	3.52 s		3.40 s

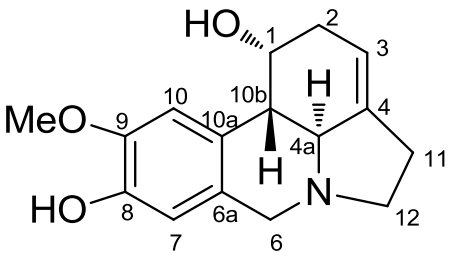

Figure S35. Structure of norpluviine (**14**).

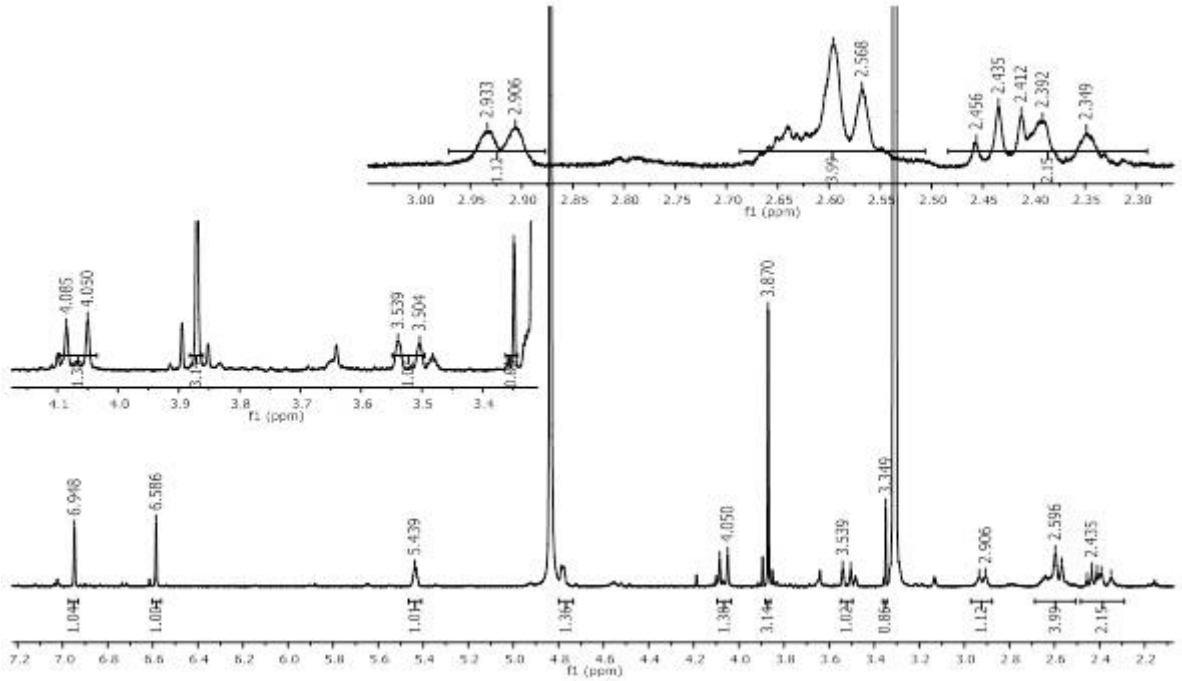

Figure S36. ^{1}H NMR spectrum (400 MHz, CD_3OD) of norpluviine (**14**).

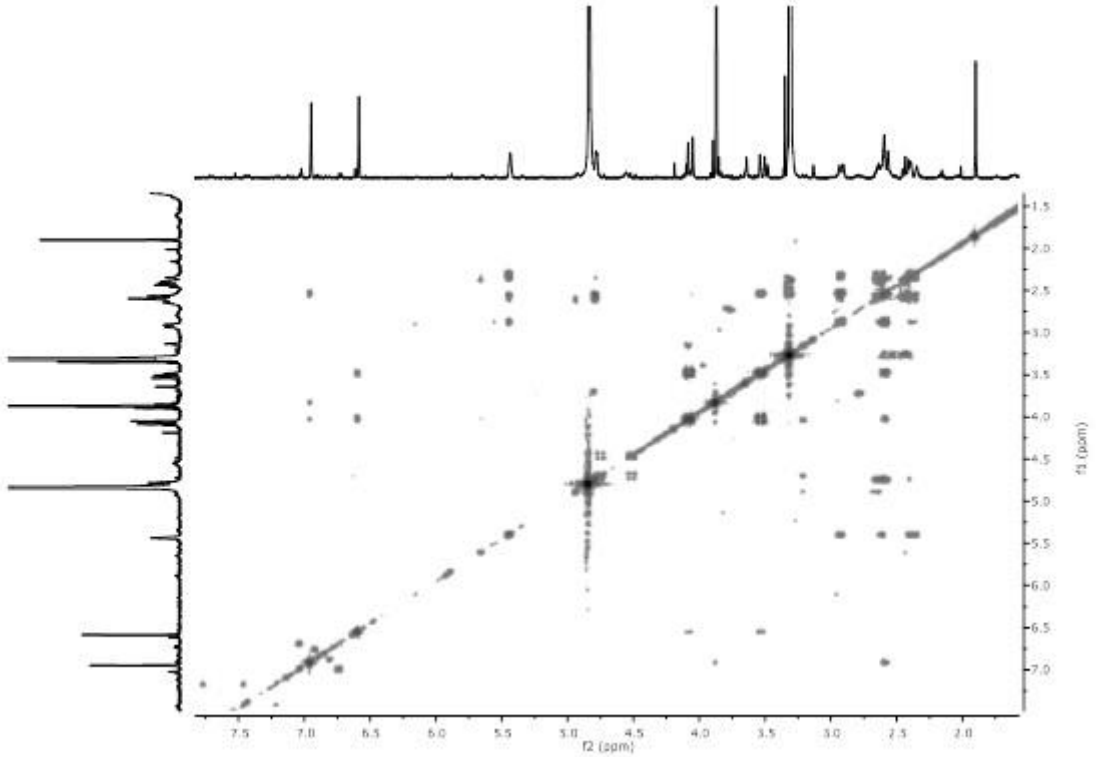

Figure S37. ^{1}H-^{1}H correlation spectroscopy (COSY) spectrum (400 MHz, CD_3OD) of norpluviine(**14**).

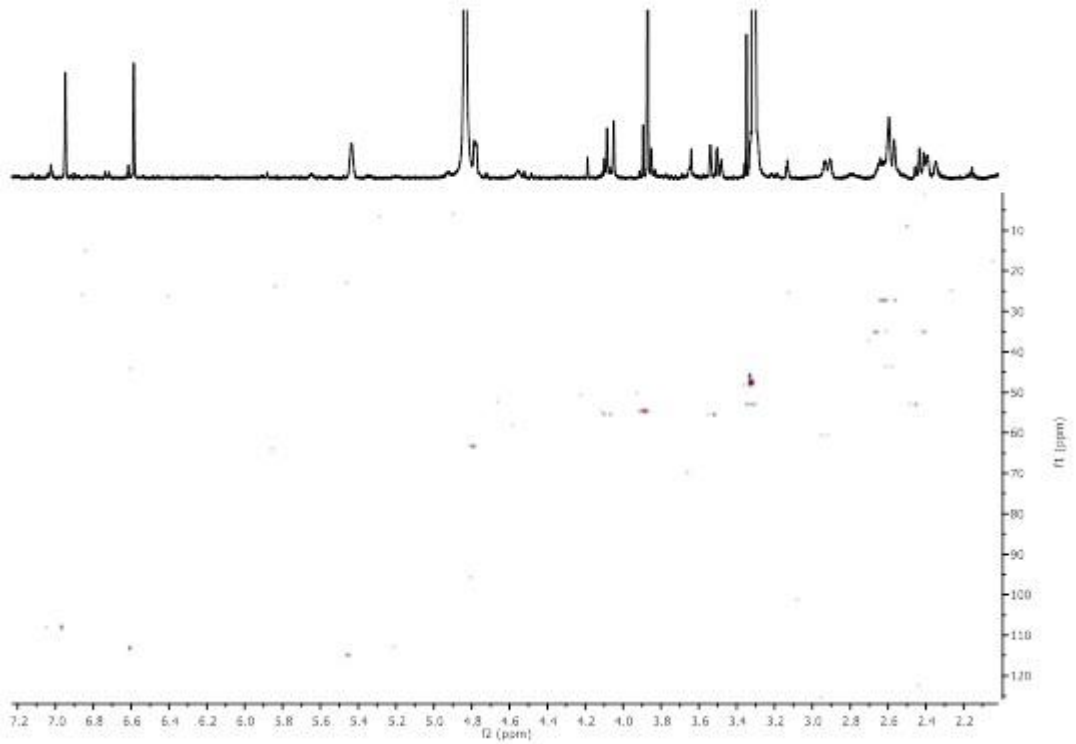

Figure S38. Heteronuclear single-quantum correlation (HSQC) spectrum (400 MHz, CD_3OD) of norpluviine (**14**).

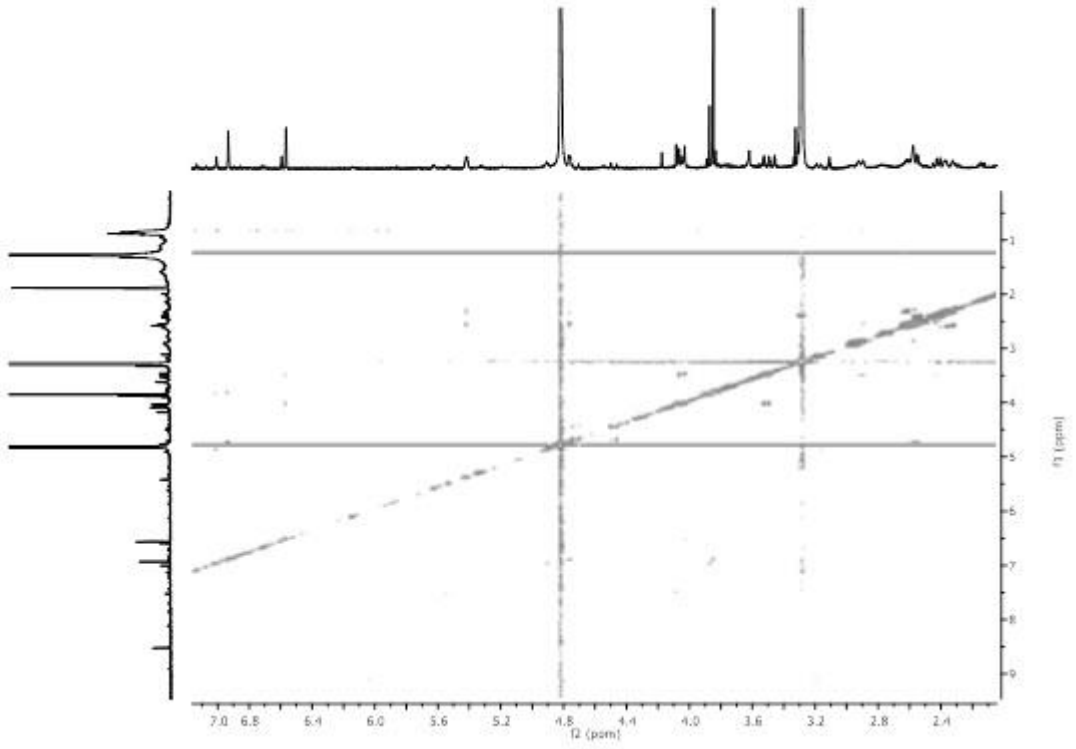

Figure S39. ^{1}H-^{1}H correlation spectroscopy (NOESY) spectrum (400 MHz, CD_3OD) of norpluviine (**14**).

Table S9. ^{1}H NMR (400 MHz, CD_3OD,) data of norpluviine (**14**) compared with the literature (400 MHz, $CDCl_3$)[6]

Position	δ_H (*J* in Hz) Compound **14**	δ_H (*J* in Hz) literature
1	4.76-4.80 m	4.26 dd (5.9, 1.0)
2α	2.51-2.67 m	2.62 m
2β	2.31-2.47 m	2.33 m
3	5.44 br d (2.8)	5.39 d (2.2)
4a	2.92 d (10.8)	2.76 d (9.9)
6α	3.52 d (14.0)	3.50 d (14.5)
6β	4.07 d (14.0)	4.13 d (14.5)
7	6.59 s	6.64 s
10	6.95 s	6.74 s
10b	2.51-2.67 m	2.66 d (9.9)
11α	2.51-2.67 m	2.59 m
11β	2.51-2.67 m	2.59 m
12α	2.31-2.47 m	2.37 m
12β	3.32-3.34 m	3.34 m

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