## **Supplementary Information**

## Stephapierrines A–H, new tetrahydroprotoberberine and aporphine alkaloids from the tubers of *Stephania pierrei* Diels and their anti-cholinesterase activities

Waraluck Chaichompoo,<sup>a</sup> Pornchai Rojsitthisak,<sup>\*a,b</sup> Wachirachai Pabuprapap,<sup>c</sup> Yuttana Siriwattanasathien,<sup>c</sup> Pathumwadee Yotmanee,<sup>c</sup> Woraphot Haritakun<sup>d</sup> and Apichart Suksamrarn<sup>c</sup>

<sup>a</sup>Department of Food and Pharmaceutical Chemistry, Faculty of Pharmaceutical Sciences, Chulalongkorn University, Bangkok 10330, Thailand <sup>b</sup>Natural Products for Aging and Chronic Diseases Research Unit, Chulalongkorn University, Bangkok 10330, Thailand <sup>c</sup>Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Ramkhamhaeng University, Bangkok 10240, Thailand <sup>d</sup>Program in Chemical Technology, Faculty of Science and Technology, Suan Dusit University, Bangkok 10700, Thailand \* Correspondence: pornchai.r@chula.ac.th; Tel.: +66-2-218-8310; Fax: +66-2-254-5195

## List of Figures

Figure	Contents	Page
S1. <sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz)	of stephapierrine A (1)	10
<b>S2.</b> Expansion of <sup>1</sup> H NMR spectrum (CDC)	3, 400 MHz) of stephapierrine A (1) (1)	10
<b>S3.</b> Expansion of <sup>1</sup> H NMR spectrum (CDC)	3, 400 MHz) of stephapierrine A (1) (2)	11
S4. <sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz)	of stephapierrine A (1)	11
S5. DEPT135 spectrum (CDCl <sub>3</sub> , 100 MHz)	of stephapierrine A (1)	12
<b>S6.</b> COSY spectrum of stephapierrine A (1)	in CDCl <sub>3</sub>	12
<b>S7.</b> Expansion of COSY spectrum of stepha	pierrine A (1) in $CDCl_3$	13
<b>S8.</b> HMQC spectrum of stephapierrine A (1)	in CDCl <sub>3</sub>	13
<b>S9.</b> Expansion of HMQC spectrum of steph	apierrine A (1) in CDCl <sub>3</sub> (1)	14
S10. Expansion of HMQC spectrum of step	hapierrine A (1) in $CDCl_3(2)$	14
<b>S11.</b> HMBC spectrum of stephapierrine A (	1) in CDCl <sub>3</sub>	15
S12. Expansion of HMBC spectrum of step	hapierrine A (1) in $CDCl_3(1)$	15
S13. Expansion of HMBC spectrum of step	hapierrine A (1) in $CDCl_3(2)$	16
S14. Expansion of HMBC spectrum of step	hapierrine A (1) in $CDCl_3(3)$	16
<b>S15.</b> NOESY spectrum of stephapierrine A	(1) in CDCl <sub>3</sub>	17
S16. Expansion of NOESY spectrum of ste	phapierrine A (1) in CDCl <sub>3</sub> (1)	17
S17. Expansion of NOESY spectrum of ste	phapierrine A (1) in CDCl <sub>3</sub> (2)	18
<b>S18.</b> ESI-TOF-MS of stephapierrine A (1)		18
<b>S19.</b> IR spectrum of stephapierrine A (1)		19
<b>S20.</b> <sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz)	of stephapierrine B (2)	19
<b>S21.</b> Expansion of <sup>1</sup> H NMR spectrum (CDC	$Cl_3$ , 400 MHz) of stephapierrine B ( <b>2</b> ) (1)	20
<b>S22.</b> Expansion of <sup>1</sup> H NMR spectrum (CDC	$Cl_3$ , 400 MHz) of stephapierrine B ( <b>2</b> ) (2)	20
<b>S23.</b> <sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz	) of stephapierrine B ( <b>2</b> )	21
S24. DEPT135 spectrum (CDCl <sub>3</sub> , 100 MHz	z) of stephapierrine B (2)	21
<b>S25.</b> COSY spectrum of stephapierrine B (2)	in CDCl <sub>3</sub>	22
<b>S26.</b> Expansion of COSY spectrum of steph	hapierrine B (2) in CDCl <sub>3</sub>	22
<b>S27.</b> HMQC spectrum of stephapierrine B (2	) in CDCl <sub>3</sub>	23
<b>S28.</b> Expansion of HMQC spectrum of step	hapierrine B ( $2$ ) in CDCl <sub>3</sub> (1)	23
<b>S29.</b> Expansion of HMQC spectrum of step	hapierrine B ( $2$ ) in CDCl <sub>3</sub> ( $2$ )	24
<b>S30.</b> HMBC spectrum of stephapierrine B (	<b>2</b> ) in CDCl <sub>3</sub>	24
<b>S31.</b> Expansion of HMBC spectrum of step	hapierrine B (2) in $CDCl_3(1)$	25

Figure	Contents	Page
<b>S32.</b> Expansion of HMBC spectrum of s	tephapierrine B ( <b>2</b> ) in CDCl <sub>3</sub> (2)	25
<b>\$33.</b> Expansion of HMBC spectrum of s	tephapierrine B $(2)$ in CDCl <sub>3</sub> $(3)$	26
<b>\$34.</b> NOESY spectrum of stephapierrine	B ( <b>2</b> ) in CDCl <sub>3</sub>	26
<b>\$35.</b> Expansion of NOESY spectrum of	stephapierrine B ( $2$ ) in CDCl <sub>3</sub> (1)	27
<b>\$36.</b> Expansion of NOESY spectrum of	stephapierrine B ( $2$ ) in CDCl <sub>3</sub> (2)	27
<b>\$37.</b> ESI-TOF-MS of stephapierrine B (2)	2)	28
<b>\$38.</b> IR spectrum of stephapierrine B (2)		28
<b>\$39.</b> <sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MI	Hz) of stephapierrine C ( <b>3</b> )	29
<b>S40.</b> Expansion of <sup>1</sup> H NMR spectrum (C	$DCl_3$ , 400 MHz) of stephapierrine C (3) (1)	29
<b>S41.</b> Expansion of <sup>1</sup> H NMR spectrum (C	$DCl_3$ , 400 MHz) of stephapierrine C (3) (2)	30
<b>S42.</b> <sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 M	Hz) of stephapierrine C ( <b>3</b> )	30
<b>\$43.</b> DEPT135 spectrum (CDCl <sub>3</sub> , 100 M	Hz) of stephapierrine C ( <b>3</b> )	31
<b>\$44.</b> COSY spectrum of stephapierrine C	C(3) in CDCl <sub>3</sub>	31
<b>S45.</b> Expansion of COSY spectrum of st	ephapierrine C ( <b>3</b> ) in CDCl <sub>3</sub>	32
<b>S46.</b> HMQC spectrum of stephapierrine	C ( <b>3</b> ) in CDCl <sub>3</sub>	32
<b>S47.</b> Expansion of HMQC spectrum of s	tephapierrine C ( <b>3</b> ) in CDCl <sub>3</sub> (1)	33
<b>S48.</b> Expansion of HMQC spectrum of s	tephapierrine C ( <b>3</b> ) in CDCl <sub>3</sub> (2)	33
<b>S49.</b> HMBC spectrum of stephapierrine	$C(3)$ in $CDCl_3$	34
<b>\$50.</b> Expansion of HMBC spectrum of s	tephapierrine C ( <b>3</b> ) in CDCl <sub>3</sub> (1)	34
<b>S51.</b> Expansion of HMBC spectrum of s	tephapierrine C ( <b>3</b> ) in CDCl <sub>3</sub> (2)	35
<b>S52.</b> NOESY spectrum of stephapierrine	C ( <b>3</b> ) in CDCl <sub>3</sub>	35
<b>\$53.</b> Expansion of NOESY spectrum of	stephapierrine C ( <b>3</b> ) in $CDCl_3(1)$	36
<b>S54.</b> Expansion of NOESY spectrum of	stephapierrine C ( <b>3</b> ) in $CDCl_3(2)$	36
<b>\$55.</b> ESI-TOF-MS of stephapierrine C (	3)	37
<b>S56.</b> IR spectrum of stephapierrine C (3)		37
<b>S57.</b> <sup>1</sup> H NMR spectrum (CD <sub>3</sub> OD, 400 M	(Hz) of stephapierrine D (4)	38
<b>\$58.</b> Expansion of <sup>1</sup> H NMR spectrum (C	D <sub>3</sub> OD, 400 MHz) of stephapierrine D (4) (1)	38
<b>\$59.</b> Expansion of <sup>1</sup> H NMR spectrum (C	D <sub>3</sub> OD, 400 MHz) of stephapierrine D (4) (2)	39
<b>S60.</b> Expansion of <sup>1</sup> H NMR spectrum (C	D <sub>3</sub> OD, 400 MHz) of stephapierrine D (4) (3)	39
<b>S61.</b> <sup>13</sup> C NMR spectrum (CD <sub>3</sub> OD, 100 M	(4) AHz) of stephapierrine D	40
<b>S62.</b> DEPT135 spectrum (CD <sub>3</sub> OD, 100 N	MHz) of stephapierrine D (4)	40
<b>S63.</b> COSY spectrum of stephapierrine I	O(4) in CD <sub>3</sub> OD	41
<b>S64.</b> Expansion of COSY spectrum of st	ephapierrine D (4) in CD <sub>3</sub> OD	41

Figure     Contents		Page
<b>S65.</b> Expansion of COSY spectrum of stephapierrine D	(4) in CD <sub>3</sub> OD	42
<b>S66.</b> HMQC spectrum of stephapierrine D (4) in CD <sub>3</sub> O	D	42
<b>S67.</b> Expansion of HMQC spectrum of stephapierrine D	<b>O</b> ( <b>4</b> ) in CD <sub>3</sub> OD (1)	43
<b>S68.</b> Expansion of HMQC spectrum of stephapierrine D	<b>O</b> (4) in CD <sub>3</sub> OD (2)	43
<b>S69.</b> HMBC spectrum of stephapierrine D (4) in CD <sub>3</sub> Ol	)	44
<b>S70.</b> Expansion of HMBC spectrum of stephapierrine D	<b>0</b> (4) in CD <sub>3</sub> OD (1)	44
<b>S71.</b> Expansion of HMBC spectrum of stephapierrine D	<b>0</b> (4) in CD <sub>3</sub> OD (2)	45
<b>S72.</b> Expansion of HMBC spectrum of stephapierrine D	<b>O</b> (4) in CD <sub>3</sub> OD (3)	45
<b>S73.</b> Expansion of HMBC spectrum of stephapierrine D	<b>0</b> ( <b>4</b> ) in CD <sub>3</sub> OD (4)	46
<b>S74.</b> NOESY spectrum of stephapierrine D (4) in CD <sub>3</sub> C	D	46
S75. Expansion of NOESY spectrum of stephapierrine	D (4) in CD <sub>3</sub> OD (1)	47
<b>S76.</b> Expansion of NOESY spectrum of stephapierrine	D (4) in CD <sub>3</sub> OD (2)	47
S77. ESI-TOF-MS of stephapierrine D (4)		48
<b>S78.</b> IR spectrum of stephapierrine D (4)		48
<b>S79.</b> <sup>1</sup> H NMR spectrum (CD <sub>3</sub> OD, 400 MHz) of stephap	ierrine E (5)	49
<b>S80.</b> Expansion of <sup>1</sup> H NMR spectrum (CD <sub>3</sub> OD, 400 MI	Hz) of stephapierrine E (5) (1)	49
<b>S81.</b> Expansion of <sup>1</sup> H NMR spectrum (CD <sub>3</sub> OD, 400 MI	Hz) of stephapierrine E (5) (2)	50
<b>S82.</b> <sup>13</sup> C NMR spectrum (CD <sub>3</sub> OD, 100 MHz) of stephap	pierrine E (5)	50
S83. DEPT135 spectrum (CD <sub>3</sub> OD, 100 MHz) of stepha	pierrine E (5)	51
<b>S84.</b> COSY spectrum of stephapierrine E ( <b>5</b> ) in CD <sub>3</sub> OD	)	51
<b>S85.</b> Expansion of COSY spectrum of stephapierrine E	( <b>5</b> ) in CD <sub>3</sub> OD (1)	52
<b>S86.</b> Expansion of COSY spectrum of stephapierrine E	( <b>5</b> ) in CD <sub>3</sub> OD (2)	52
<b>S87.</b> HMQC spectrum of stephapierrine E (5) in CD <sub>3</sub> OI	)	53
<b>S88.</b> Expansion of HMQC spectrum of stephapierrine E	E (5) in CD <sub>3</sub> OD (1)	53
<b>S89.</b> Expansion of HMQC spectrum of stephapierrine E	E ( <b>5</b> ) in CD <sub>3</sub> OD (2)	54
<b>S90.</b> HMBC spectrum of stephapierrine E (5) in CD <sub>3</sub> OI	)	54
<b>S91.</b> Expansion of HMBC spectrum of stephapierrine E	(5) in CD <sub>3</sub> OD (1)	55
<b>S92.</b> Expansion of HMBC spectrum of stephapierrine E	(5) in CD <sub>3</sub> OD (2)	55
<b>S93.</b> Expansion of HMBC spectrum of stephapierrine E	(5) in CD <sub>3</sub> OD (3)	56
<b>S94.</b> NOESY spectrum of stephapierrine E (5) in CD <sub>3</sub> O	D	56
<b>S95.</b> Expansion of NOESY spectrum of stephapierrine	$E(5)$ in $CD_3OD$	57
<b>S96.</b> ESI-TOF-MS of stephapierrine E (5)		57
<b>S97.</b> IR spectrum of stephapierrine E (5)		58

_	
-	
_	
$\sim$	

Figure	Contents	Page
<b>S98.</b> <sup>1</sup> H NMR spectre	um (CD <sub>3</sub> OD, 400 MHz) of stephapierrine F (6)	58
<b>S99.</b> Expansion of <sup>1</sup> H	I NMR spectrum (CD <sub>3</sub> OD, 400 MHz) of stephapierrine F (6) (1)	59
<b>S100.</b> Expansion of <sup>1</sup>	H NMR spectrum (CD <sub>3</sub> OD, 400 MHz) of stephapierrine F (6) (2)	59
<b>S101.</b> Expansion of <sup>1</sup>	H NMR spectrum (CD <sub>3</sub> OD, 400 MHz) of stephapierrine F (6) (3)	60
<b>S102.</b> <sup>13</sup> C NMR spec	trum (CD <sub>3</sub> OD, 100 MHz) of stephapierrine F (6)	60
<b>S103.</b> DEPT135 spec	ctrum (CD <sub>3</sub> OD, 100 MHz) of stephapierrine F (6)	61
S104. COSY spectru	m of stephapierrine F (6) in CD <sub>3</sub> OD	61
<b>S105.</b> Expansion of <b>G</b>	COSY spectrum of stephapierrine F (6) in CD <sub>3</sub> OD (1)	62
<b>S106.</b> Expansion of <b>G</b>	COSY spectrum of stephapierrine F (6) in CD <sub>3</sub> OD (2)	62
S107. HMQC spectru	um of stephapierrine F (6) in CD <sub>3</sub> OD	63
<b>S108.</b> Expansion of H	HMQC spectrum of stephapierrine F (6) in CD <sub>3</sub> OD (1)	63
<b>S109.</b> Expansion of H	HMQC spectrum of stephapierrine F (6) in CD <sub>3</sub> OD (2)	64
S110. HMBC spectru	um of stephapierrine F (6) in CD <sub>3</sub> OD	64
<b>S111.</b> Expansion of H	HMBC spectrum of stephapierrine F (6) in CD <sub>3</sub> OD (1)	65
<b>S112.</b> Expansion of H	HMBC spectrum of stephapierrine F (6) in CD <sub>3</sub> OD (2)	65
<b>S113.</b> Expansion of H	HMBC spectrum of stephapierrine F (6) in CD <sub>3</sub> OD (3)	66
<b>S114.</b> Expansion of H	HMBC spectrum of stephapierrine F (6) in CD <sub>3</sub> OD (4)	66
S115. NOESY spectr	rum of stephapierrine F (6) in CD <sub>3</sub> OD	67
<b>S116.</b> Expansion of M	NOESY spectrum of stephapierrine F (6) in CD <sub>3</sub> OD (1)	67
<b>S117.</b> Expansion of M	NOESY spectrum of stephapierrine F (6) in CD <sub>3</sub> OD (2)	68
S118. ESI-TOF-MS	of stephapierrine F (6)	68
S119. IR spectrum of	f stephapierrine F (6)	69
S120. <sup>1</sup> H NMR spect	rum (CD <sub>3</sub> OD, 400 MHz) of stephapierrine G (7)	69
<b>S121.</b> Expansion of <sup>1</sup>	H NMR spectrum (CD <sub>3</sub> OD, 400 MHz) of stephapierrine G (7) (1)	70
<b>S122.</b> Expansion of <sup>1</sup>	H NMR spectrum (CD <sub>3</sub> OD, 400 MHz) of stephapierrine G (7) (2)	70
<b>S123.</b> <sup>13</sup> C NMR spec	trum (CD <sub>3</sub> OD, 100 MHz) of stephapierrine G (7)	71
<b>S124.</b> DEPT135 spec	ctrum (CD <sub>3</sub> OD, 100 MHz) of stephapierrine G (7)	71
S125. COSY spectru	m of stephapierrine G (7) in CD <sub>3</sub> OD	72
S126. HMQC spectru	um of stephapierrine G (7) in CD <sub>3</sub> OD	72
S127. HMBC spectru	um of stephapierrine G (7) in CD <sub>3</sub> OD	73
<b>S128.</b> Expansion of I	HMBC spectrum of stephapierrine G (7) in CD <sub>3</sub> OD	73
S129. NOESY spectr	rum of stephapierrine G (7) in CD <sub>3</sub> OD	74
S130. ESI-TOF-MS	of stephapierrine G (7)	74

Figure Contents	Page
<b>S131.</b> IR spectrum of stephapierrine G (7)	75
<b>S132.</b> <sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of stephapierrine H (8)	75
<b>S133.</b> Expansion of <sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of stephapierrine H (8) (1)	76
<b>S134.</b> Expansion of <sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of stephapierrine H (8) (2)	76
<b>S135.</b> <sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of stephapierrine H (8)	77
<b>\$136.</b> DEPT135 spectrum (CDCl <sub>3</sub> , 100 MHz) of stephapierrine H (8)	77
<b>\$137.</b> COSY spectrum of stephapierrine H (8) in CDCl <sub>3</sub>	78
<b>\$138.</b> HMQC spectrum of stephapierrine H (8) in CDCl <sub>3</sub>	78
<b>S139.</b> Expansion of HMQC spectrum of stephapierrine H (8) in $CDCl_3$	79
<b>S140.</b> HMBC spectrum of stephapierrine H (8) in CDCl <sub>3</sub>	79
<b>S141.</b> Expansion of HMBC spectrum of stephapierrine H $(8)$ in CDCl <sub>3</sub>	80
<b>S142.</b> NOESY spectrum of stephapierrine H (8) in CDCl <sub>3</sub>	80
<b>S143.</b> ESI-TOF-MS of stephapierrine H (8)	81
<b>S144.</b> IR spectrum of stephapierrine H (8)	81
<b>S145.</b> <sup>1</sup> H NMR spectrum (CD <sub>3</sub> OD, 400 MHz) of <i>O</i> , <i>N</i> -diacetylasimilobine (9)	82
<b>S146.</b> <sup>13</sup> C NMR spectrum (CD <sub>3</sub> OD, 100 MHz) of <i>O</i> , <i>N</i> -diacetylasimilobine (9)	82
<b>\$147.</b> DEPT135 spectrum (CD <sub>3</sub> OD, 100 MHz) of <i>O</i> , <i>N</i> -diacetylasimilobine (9)	83
<b>\$148.</b> COSY spectrum of <i>O</i> , <i>N</i> -diacetylasimilobine (9) in CD <sub>3</sub> OD	83
<b>\$149.</b> HMQC spectrum of <i>O</i> , <i>N</i> -diacetylasimilobine (9) in CD <sub>3</sub> OD	84
<b>\$150.</b> HMBC spectrum of <i>O</i> , <i>N</i> -diacetylasimilobine (9) in CD <sub>3</sub> OD	84
<b>\$151.</b> NOESY spectrum of <i>O</i> , <i>N</i> -diacetylasimilobine (9) in CD <sub>3</sub> OD	85
<b>\$152.</b> <sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of <i>N</i> -acetamidesecocrebanine ( <b>10</b> )	85
<b>S153.</b> <sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of <i>N</i> -acetamidesecocrebanine (10)	86
<b>\$154.</b> DEPT135 spectrum (CDCl <sub>3</sub> , 100 MHz) of <i>N</i> -acetamidesecocrebanine (10)	86
<b>\$155.</b> COSY spectrum of <i>N</i> -acetamidesecocrebanine (10) in CDCl <sub>3</sub>	87
<b>S156.</b> HMQC spectrum of $N$ -acetamidesecocrebanine (10) in CDCl <sub>3</sub>	87
<b>S157.</b> HMBC spectrum of $N$ -acetamidesecocrebanine (10) in CDCl <sub>3</sub>	88
<b>\$158.</b> NOESY spectrum of <i>N</i> -acetamidesecocrebanine (10) in CDCl <sub>3</sub>	88
<b>\$159.</b> <sup>1</sup> H NMR spectrum (DMSO- <i>d</i> <sub>6</sub> , 400 MHz) of 2,3-didemethyltetrahydropalmatine ( <b>11</b> )	89
<b>S160.</b> <sup>13</sup> C NMR spectrum (DMSO- <i>d</i> <sub>6</sub> , 100 MHz) of 2,3-didemethyltetrahydropalmatine ( <b>11</b> )	89
<b>S161.</b> DEPT135 spectrum (DMSO- $d_6$ , 100 MHz) of 2,3-didemethyltetrahydropalmatine (11)	90
<b>S162.</b> COSY spectrum of 2,3-didemethyltetrahydropalmatine (11) in DMSO- $d_6$	90
<b>S163.</b> HMQC spectrum of 2,3-didemethyltetrahydropalmatine (11) in DMSO- $d_6$	91

Figure	Contents	Page
S164. HMBC spectrun	n of 2,3-didemethyltetrahydropalmatine (11) in DMSO- $d_6$	91
S165. NOESY spectru	m of 2,3-didemethyltetrahydropalmatine (11) in DMSO- $d_6$	92
<b>S166.</b> <sup>1</sup> H NMR spectru	um (CD <sub>3</sub> OD, 400 MHz) of stepholidine ( <b>12</b> )	92
<b>S167.</b> <sup>13</sup> C NMR spectr	um (CD <sub>3</sub> OD, 100 MHz) of stepholidine ( <b>12</b> )	93
S168. <sup>1</sup> H NMR spectru	m (CD <sub>3</sub> OD, 400 MHz) of discretamine (13)	93
<b>S169.</b> <sup>13</sup> C NMR spectr	um (CD <sub>3</sub> OD, 100 MHz) of discretamine (13)	94
<b>S170.</b> <sup>1</sup> H NMR spectru	um (CDCl <sub>3</sub> , 400 MHz) of tetrahydropalmatine (14)	94
<b>S171.</b> <sup>13</sup> C NMR spectr	um (CDCl <sub>3</sub> , 100 MHz) of tetrahydropalmatine (14)	95
<b>S172.</b> <sup>1</sup> H NMR spectru	um (CD <sub>3</sub> OD, 400 MHz) of <i>N</i> -methylstepholidine ( <b>15</b> )	95
<b>S173.</b> <sup>13</sup> C NMR spectr	um (CD <sub>3</sub> OD, 100 MHz) of <i>N</i> -methylstepholidine ( <b>15</b> )	96
<b>S174.</b> <sup>1</sup> H NMR spectru	um (CD <sub>3</sub> OD, 400 MHz) of cyclanoline (16)	96
<b>S175.</b> <sup>13</sup> C NMR spectr	um (CD <sub>3</sub> OD, 100 MHz) of cyclanoline (16)	97
<b>S176.</b> <sup>1</sup> H NMR spectru	um (CDCl <sub>3</sub> + 5 drops CD <sub>3</sub> OD, 400 MHz) of <i>N</i> -methyltetrahydro-	97
palmatine (17)		
<b>S177.</b> <sup>13</sup> C NMR spectr	um (CDCl <sub>3</sub> + 5 drops CD <sub>3</sub> OD, 100 MHz) of <i>N</i> -methyltetrahydro-	98
palmatine (17)		
<b>S178.</b> <sup>1</sup> H NMR spectru	um (CD <sub>3</sub> OD, 400 MHz) of jatrorrhizine ( <b>18</b> )	98
<b>S179.</b> <sup>13</sup> C NMR spectr	um (CD <sub>3</sub> OD, 100 MHz) of jatrorrhizine (18)	99
<b>S180.</b> <sup>1</sup> H NMR spectru	um (DMSO- <i>d</i> <sub>6</sub> , 400 MHz) of palmatine ( <b>19</b> )	99
<b>S181.</b> <sup>13</sup> C NMR spectr	um (DMSO- $d_6$ , 100 MHz) of palmatine (19)	100
<b>S182.</b> <sup>1</sup> H NMR spectru	um (CDCl <sub>3</sub> , 400 MHz) of dehydrocorydaline (20)	100
<b>S183.</b> <sup>13</sup> C NMR spectr	um (CDCl <sub>3</sub> , 100 MHz) of dehydrocorydaline (20)	101
<b>S184.</b> <sup>1</sup> H NMR spectru	um (CD <sub>3</sub> OD, 400 MHz) of pseudodehydrocorydaline (21)	101
S185. <sup>13</sup> C NMR spectr	um (CD <sub>3</sub> OD, 100 MHz) of pseudodehydrocorydaline ( <b>21</b> )	102
<b>S186.</b> <sup>1</sup> H NMR spectru	um (CDCl <sub>3</sub> , 400 MHz) of roemerine ( <b>22</b> )	102
<b>S187.</b> <sup>13</sup> C NMR spectr	um (CDCl <sub>3</sub> , 100 MHz) of roemerine ( <b>22</b> )	103
S188. <sup>1</sup> H NMR spectru	um (CDCl <sub>3</sub> , 400 MHz) of (-)-stephanine ( <b>23</b> )	103
<b>S189.</b> <sup>13</sup> C NMR spectr	um (CDCl <sub>3</sub> , 100 MHz) of (–)-stephanine ( <b>23</b> )	104
<b>S190.</b> <sup>1</sup> H NMR spectru	um (CDCl <sub>3</sub> , 400 MHz) of (-)-isolaureline ( <b>24</b> )	104
<b>S191.</b> <sup>13</sup> C NMR spectr	um (CDCl <sub>3</sub> , 100 MHz) of (-)-isolaureline (24)	105
<b>S192.</b> <sup>1</sup> H NMR spectru	um (CDCl <sub>3</sub> , 400 MHz) of crebanine ( <b>25</b> )	105
<b>S193.</b> <sup>13</sup> C NMR spectr	um (CDCl <sub>3</sub> , 100 MHz) of crebanine ( <b>25</b> )	106
S194 <sup>1</sup> H NMR spectra	$m (CDCl_3 + 5 drops CD_3OD, 400 MHz) of dicentrine (26)$	106

Figure	e Contents	Page
S195.	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> + 5 drops CD <sub>3</sub> OD, 100 MHz) of dicentrine ( <b>26</b> )	107
S196.	<sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of (-)-ushinsunine (27)	107
S197.	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of (-)-ushinsunine (27)	108
S198.	<sup>1</sup> H NMR spectrum (CD <sub>3</sub> OD, 400 MHz) of (-)-ayuthianine ( <b>28</b> )	108
S199.	<sup>13</sup> C NMR spectrum (CD <sub>3</sub> OD, 100 MHz) of (-)-ayuthianine (28)	109
S200.	<sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of sukhodianine ( <b>29</b> )	109
S201.	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of sukhodianine (29)	110
S202.	<sup>1</sup> H NMR spectrum (Acetone- <i>d</i> <sub>6</sub> , 400 MHz) of (–)- <i>N</i> -fonnylanonaine ( <b>30</b> )	110
S203.	<sup>13</sup> C NMR spectrum (Acetone- <i>d</i> <sub>6</sub> , 100 MHz) of (–)- <i>N</i> -fonnylanonaine ( <b>30</b> )	111
S204.	<sup>1</sup> H NMR spectrum (CD <sub>3</sub> OD, 400 MHz) of (-)- <i>N</i> -methylasimilobine ( <b>31</b> )	111
S205.	<sup>13</sup> C NMR spectrum (CD <sub>3</sub> OD, 100 MHz) of (-)- <i>N</i> -methylasimilobine ( <b>31</b> )	112
S206.	<sup>1</sup> H NMR spectrum (CD <sub>3</sub> OD, 400 MHz) of (-)-asimilobine ( <b>32</b> )	112
S207.	<sup>13</sup> C NMR spectrum (CD <sub>3</sub> OD, 100 MHz) of (-)-asimilobine ( <b>32</b> )	113
S208.	<sup>1</sup> H NMR spectrum (CD <sub>3</sub> OD, 400 MHz) of (–)-asimilobine-2- <i>O</i> -β-D-glucoside ( <b>33</b> )	113
S209.	<sup>13</sup> C NMR spectrum (CD <sub>3</sub> OD, 100 MHz) of (–)-asimilobine-2- <i>O</i> -β-D-glucoside ( <b>33</b> )	114
S210.	<sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of lanuginosine ( <b>34</b> )	114
S211.	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of lanuginosine ( <b>34</b> )	115
S212.	<sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> + 5 drops CD <sub>3</sub> OD, 400 MHz) of dicentrinone ( <b>35</b> )	115
<b>S213</b>	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> + 5 drops CD <sub>3</sub> OD, 100 MHz) of dicentrinone ( <b>35</b> )	116
S214.	<sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of oxocrebanine ( <b>36</b> )	116
S215.	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of oxocrebanine ( <b>36</b> )	117
S216.	<sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of 8-methoxyuvoriopsine ( <b>37</b> )	117
S217.	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of 8-methoxyuvoriopsine ( <b>37</b> )	118
S218.	<sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of dehydroroemerine ( <b>38</b> )	118
S219.	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of dehydroroemerine ( <b>38</b> )	119
S220.	<sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of dehydrostephanine ( <b>39</b> )	119
S221.	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of dehydrostephanine ( <b>39</b> )	120
S222.	<sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of dehydroisolaureline ( <b>40</b> )	120
S223.	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of dehydroisolaureline ( <b>40</b> )	121
S224.	<sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of dehydrocrebanine ( <b>41</b> )	121
S225.	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of dehydrocrebanine ( <b>41</b> )	122
S226.	<sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of dehydrodicentrine ( <b>42</b> )	122
S227.	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of dehydrodicentrine ( <b>42</b> )	123

Figur	e Contents	Page
S228.	<sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of (–)-crebanine-β- <i>N</i> -oxide ( <b>43</b> )	123
S229.	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of (–)-crebanine-β- <i>N</i> -oxide ( <b>43</b> )	124
S230.	<sup>1</sup> H NMR spectrum (CD <sub>3</sub> OD, 400 MHz) of coclaurine (44)	124
S231.	<sup>13</sup> C NMR spectrum (CD <sub>3</sub> OD, 100 MHz) of coclaurine (44)	125
S232.	<sup>1</sup> H NMR spectrum (CDCl <sub>3</sub> , 400 MHz) of salutaridine (45)	125
S233.	<sup>13</sup> C NMR spectrum (CDCl <sub>3</sub> , 100 MHz) of salutaridine ( <b>45</b> )	126
S234.	ECD spectra of stephapierrines A-D (1-4)	126
S235.	ECD spectra of stephapierrines E-F (5-6) and O,N-diacetylasimilobine (9)	127

## List of Table

Table	Contents	Page
<b>S1.</b> Cholinesterase inhibitory activit	ies of aporphine alkaloids	128



Figure S2. Expansion of <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of stephapierrine A (1) (1)



Figure S3. Expansion of <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of stephapierrine A (1) (2)



Figure S4. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of stephapierrine A (1)



Figure S5. DEPT135 spectrum (CDCl<sub>3</sub>, 100 MHz) of stephapierrine A (1)



Figure S6. COSY spectrum of stephapierrine A (1) in CDCl<sub>3</sub>



Figure S7. Expansion of COSY spectrum of stephapierrine A (1) in CDCl<sub>3</sub>



Figure S8. HMQC spectrum of stephapierrine A (1) in CDCl<sub>3</sub>



Figure S9. Expansion of HMQC spectrum of stephapierrine A (1) in CDCl<sub>3</sub>(1)



Figure S10. Expansion of HMQC spectrum of stephapierrine A (1) in CDCl<sub>3</sub>(2)



Figure S11. HMBC spectrum of stephapierrine A (1) in CDCl<sub>3</sub>



Figure S12. Expansion of HMBC spectrum of stephapierrine A (1) in CDCl<sub>3</sub>(1)



Figure S13. Expansion of HMBC spectrum of stephapierrine A (1) in CDCl<sub>3</sub>(2)



Figure S14. Expansion of HMBC spectrum of stephapierrine A (1) in CDCl<sub>3</sub>(3)



Figure S15. NOESY spectrum of stephapierrine A (1) in CDCl<sub>3</sub>



Figure S16. Expansion of NOESY spectrum of stephapierrine A (1) in CDCl<sub>3</sub>(1)



Figure S17. Expansion of NOESY spectrum of stephapierrine A (1) in CDCl<sub>3</sub>(2)



Figure S18. ESI-TOF-MS of stephapierrine A (1)



Figure S19. IR spectrum of stephapierrine A (1)



Figure S20. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of stephapierrine B (2)



Figure S21. Expansion of <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of stephapierrine B (2) (1)



Figure S22. Expansion of <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of stephapierrine B (2) (2)



Figure S23. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of stephapierrine B (2)



Figure S24. DEPT135 spectrum (CDCl<sub>3</sub>, 100 MHz) of stephapierrine B (2)



Figure S25. COSY spectrum of stephapierrine B (2) in CDCl<sub>3</sub>



Figure S26. Expansion of COSY spectrum of stephapierrine B (2) in CDCl<sub>3</sub>



Figure S27. HMQC spectrum of stephapierrine B (2) in CDCl<sub>3</sub>



Figure S28. Expansion of HMQC spectrum of stephapierrine B (2) in CDCl<sub>3</sub>(1)



Figure S29. Expansion of HMQC spectrum of stephapierrine B (2) in CDCl<sub>3</sub>(2)



Figure S30. HMBC spectrum of stephapierrine B (2) in CDCl<sub>3</sub>



Figure S31. Expansion of HMBC spectrum of stephapierrine B (2) in CDCl<sub>3</sub>(1)



Figure S32. Expansion of HMBC spectrum of stephapierrine B (2) in CDCl<sub>3</sub>(2)



Figure S33. Expansion of HMBC spectrum of stephapierrine B (2) in CDCl<sub>3</sub> (3)



Figure S34. NOESY spectrum of stephapierrine B (2) in CDCl<sub>3</sub>



Figure S35. Expansion of NOESY spectrum of stephapierrine B (2) in CDCl<sub>3</sub>(1)



Figure S36. Expansion of NOESY spectrum of stephapierrine B (2) in CDCl<sub>3</sub>(2)



Figure S37. ESI-TOF-MS of stephapierrine B (2)



Figure S38. IR spectrum of stephapierrine B (2)



Figure S39. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of stephapierrine C (3)



Figure S40. Expansion of <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of stephapierrine C (3) (1)



Figure S41. Expansion of <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of stephapierrine C (3) (2)



Figure S42. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of stephapierrine C (3)



Figure S43. DEPT135 spectrum (CDCl<sub>3</sub>, 100 MHz) of stephapierrine C (3)



Figure S44. COSY spectrum of stephapierrine C (3) in CDCl<sub>3</sub>



Figure S45. Expansion of COSY spectrum of stephapierrine C (3) in CDCl<sub>3</sub>



Figure S46. HMQC spectrum of stephapierrine C (3) in CDCl<sub>3</sub>



Figure S47. Expansion of HMQC spectrum of stephapierrine C (3) in CDCl<sub>3</sub>(1)



Figure S48. Expansion of HMQC spectrum of stephapierrine C (3) in CDCl<sub>3</sub>(2)



Figure S49. HMBC spectrum of stephapierrine C (3) in CDCl<sub>3</sub>



Figure S50. Expansion of HMBC spectrum of stephapierrine C (3) in CDCl<sub>3</sub>(1)



Figure S51. Expansion of HMBC spectrum of stephapierrine C (3) in CDCl<sub>3</sub>(2)



Figure S52. NOESY spectrum of stephapierrine C (3) in CDCl<sub>3</sub>



Figure S53. Expansion of NOESY spectrum of stephapierrine C (3) in CDCl<sub>3</sub>(1)



Figure S54. Expansion of NOESY spectrum of stephapierrine C (3) in CDCl<sub>3</sub>(2)


Figure S55. ESI-TOF-MS of stephapierrine C (3)



Figure S56. IR spectrum of stephapierrine C (3)



Figure S57. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine D (4)



Figure S58. Expansion of <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine D (4) (1)



Figure S59. Expansion of <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine D (4) (2)



Figure S60. Expansion of <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine D (4) (3)



Figure S61. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD, 100 MHz) of stephapierrine D (4)



Figure S62. DEPT135 spectrum (CD<sub>3</sub>OD, 100 MHz) of stephapierrine D (4)



Figure S63. COSY spectrum of stephapierrine D (4) in CD<sub>3</sub>OD



Figure S64. Expansion of COSY spectrum of stephapierrine D (4) in CD<sub>3</sub>OD (1)



Figure S65. Expansion of COSY spectrum of stephapierrine D (4) in CD<sub>3</sub>OD (2)



Figure S66. HMQC spectrum of stephapierrine D (4) in CD<sub>3</sub>OD



Figure S67. Expansion of HMQC spectrum of stephapierrine D (4) in CD<sub>3</sub>OD (1)



Figure S68. Expansion of HMQC spectrum of stephapierrine D (4) in CD<sub>3</sub>OD (2)



Figure S69. HMBC spectrum of stephapierrine D (4) in CD<sub>3</sub>OD



Figure S70. Expansion of HMBC spectrum of stephapierrine D (4) in CD<sub>3</sub>OD (1)



Figure S71. Expansion of HMBC spectrum of stephapierrine D (4) in CD<sub>3</sub>OD (2)



Figure S72. Expansion of HMBC spectrum of stephapierrine D (4) in CD<sub>3</sub>OD (3)



Figure S73. Expansion of HMBC spectrum of stephapierrine D (4) in CD<sub>3</sub>OD (4)



Figure S74. NOESY spectrum of stephapierrine D (4) in CD<sub>3</sub>OD



Figure S75. Expansion of NOESY spectrum of stephapierrine D (4) in CD<sub>3</sub>OD (1)



Figure S76. Expansion of NOESY spectrum of stephapierrine D (4) in CD<sub>3</sub>OD (2)



Figure S77. ESI-TOF-MS of stephapierrine D (4)



Figure S78. IR spectrum of stephapierrine D (4)



Figure S79. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine E (5)



Figure S80. Expansion of <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine E (5) (1)



Figure S81. Expansion of <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine E (5) (2)



Figure S82. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD, 100 MHz) of stephapierrine E (5)



Figure S83. DEPT135 spectrum (CD<sub>3</sub>OD, 100 MHz) of stephapierrine E (5)



Figure S84. COSY spectrum of stephapierrine E (5) in CD<sub>3</sub>OD



Figure S85. Expansion of COSY spectrum of stephapierrine E (5) in CD<sub>3</sub>OD (1)



Figure S86. Expansion of COSY spectrum of stephapierrine E (5) in CD<sub>3</sub>OD (2)



Figure S87. HMQC spectrum of stephapierrine E (5) in CD<sub>3</sub>OD



Figure S88. Expansion of HMQC spectrum of stephapierrine E (5) in CD<sub>3</sub>OD (1)



Figure S89. Expansion of HMQC spectrum of stephapierrine E (5) in CD<sub>3</sub>OD (2)



Figure S90. HMBC spectrum of stephapierrine E (5) in CD<sub>3</sub>OD



Figure S91. Expansion of HMBC spectrum of stephapierrine E (5) in CD<sub>3</sub>OD (1)



Figure S92. Expansion of HMBC spectrum of stephapierrine E (5) in CD<sub>3</sub>OD (2)



Figure S93. Expansion of HMBC spectrum of stephapierrine E (5) in CD<sub>3</sub>OD (3)



Figure S94. NOESY spectrum of stephapierrine E (5) in CD<sub>3</sub>OD



Figure S95. Expansion of NOESY spectrum of stephapierrine E (5) in CD<sub>3</sub>OD



Figure S96. ESI-TOF-MS of stephapierrine E (5)



Figure S97. IR spectrum of stephapierrine E (5)



Figure S98. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine F (6)



Figure S99. Expansion of <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine F (6) (1)



Figure S100. Expansion of <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine F (6) (2)



Figure S101. Expansion of <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine F (6) (3)



Figure S102. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD, 100 MHz) of stephapierrine F (6)



Figure S103. DEPT135 spectrum (CD<sub>3</sub>OD, 100 MHz) of stephapierrine F (6)



Figure S104. COSY spectrum of stephapierrine F (6) in CD<sub>3</sub>OD



Figure S105. Expansion of COSY spectrum of stephapierrine F (6) in CD<sub>3</sub>OD (1)



Figure S106. Expansion of COSY spectrum of stephapierrine F (6) in CD<sub>3</sub>OD (2)



Figure S107. HMQC spectrum of stephapierrine F (6) in CD<sub>3</sub>OD



Figure S108. Expansion of HMQC spectrum of stephapierrine F (6) in CD<sub>3</sub>OD (1)



Figure S109. Expansion of HMQC spectrum of stephapierrine F (6) in CD<sub>3</sub>OD (2)



Figure S110. HMBC spectrum of stephapierrine F (6) in CD<sub>3</sub>OD



Figure S111. Expansion of HMBC spectrum of stephapierrine F (6) in CD<sub>3</sub>OD (1)



Figure S112. Expansion of HMBC spectrum of stephapierrine F (6) in CD<sub>3</sub>OD (2)



Figure S113. Expansion of HMBC spectrum of stephapierrine F (6) in CD<sub>3</sub>OD (3)



Figure S114. Expansion of HMBC spectrum of stephapierrine F (6) in CD<sub>3</sub>OD (4)



Figure S115. NOESY spectrum of stephapierrine F (6) in CD<sub>3</sub>OD



Figure S116. Expansion of NOESY spectrum of stephapierrine F (6) in CD<sub>3</sub>OD (1)



Figure S117. Expansion of NOESY spectrum of stephapierrine F (6) in CD<sub>3</sub>OD (2)



Figure S118. ESI-TOF-MS of stephapierrine F (6)



Figure S119. IR spectrum of stephapierrine F (6)



Figure S120. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine G (7)



Figure S121. Expansion of <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine G (7) (1)



Figure S122. Expansion of <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stephapierrine G (7) (2)



Figure S123. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD, 100 MHz) of stephapierrine G (7)



Figure S124. DEPT135 spectrum (CD<sub>3</sub>OD, 100 MHz) of stephapierrine G (7)



Figure S125. COSY spectrum of stephapierrine G (7) in CD<sub>3</sub>OD



Figure S126. HMQC spectrum of stephapierrine G (7) in CD<sub>3</sub>OD


Figure S127. HMBC spectrum of stephapierrine G (7) in CD<sub>3</sub>OD



Figure S128. Expansion of HMBC spectrum of stephapierrine G (7) in CD<sub>3</sub>OD







Figure S130. ESI-TOF-MS of stephapierrine G (7)



Figure S131. IR spectrum of stephapierrine G (7)



Figure S132. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of stephapierrine H (8)



Figure S133. Expansion of <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of stephapierrine H (8) (1)



Figure S134. Expansion of <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of stephapierrine H (8) (2)

## 76



Figure S135. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of stephapierrine H (8)



Figure S136. DEPT135 spectrum (CDCl<sub>3</sub>, 100 MHz) of stephapierrine H (8)



Figure S137. COSY spectrum of stephapierrine H (8) in CDCl<sub>3</sub>



Figure S138. HMQC spectrum of stephapierrine H (8) in CDCl<sub>3</sub>



Figure S139. Expansion of HMQC spectrum of stephapierrine H (8) in CDCl<sub>3</sub>



Figure S140. HMBC spectrum of stephapierrine H (8) in CDCl<sub>3</sub>



Figure S141. Expansion of HMBC spectrum of stephapierrine H (8) in CDCl<sub>3</sub>



Figure S142. NOESY spectrum of stephapierrine H (8) in CDCl<sub>3</sub>



Figure S143. ESI-TOF-MS of stephapierrine H (8)



Figure S144. IR spectrum of stephapierrine H (8)



Figure S145. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of *O*,*N*-diacetylasimilobine (9)



Figure S146. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD, 100 MHz) of *O*,*N*-diacetylasimilobine (9)



Figure S147. DEPT135 spectrum (CD<sub>3</sub>OD, 100 MHz) of O,N-diacetylasimilobine (9)



Figure S148. COSY spectrum of O,N-diacetylasimilobine (9) in CD<sub>3</sub>OD



Figure S149. HMQC spectrum of O,N-diacetylasimilobine (9) in CD<sub>3</sub>OD



Figure S150. HMBC spectrum of O,N-diacetylasimilobine (9) in CD<sub>3</sub>OD



Figure S151. NOESY spectrum of O,N-diacetylasimilobine (9) in CD<sub>3</sub>OD



Figure S152. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of *N*-acetamidesecocrebanine (10)



Figure S154. DEPT135 spectrum (CDCl<sub>3</sub>, 100 MHz) of N-acetamidesecocrebanine (10)



Figure S155. COSY spectrum of N-acetamidesecocrebanine (10) in CDCl<sub>3</sub>



Figure S156. HMQC spectrum of N-acetamidesecocrebanine (10) in CDCl<sub>3</sub>



Figure S157. HMBC spectrum of N-acetamidesecocrebanine (10) in CDCl<sub>3</sub>



Figure S158. NOESY spectrum of N-acetamidesecocrebanine (10) in CDCl<sub>3</sub>





didemethyltetrahydropalmatine (11)



Figure S160. <sup>13</sup>C NMR spectrum (DMSO-*d*<sub>6</sub>, 100 MHz) of 2,3-

didemethyltetrahydropalmatine (11)



Figure S161. DEPT135 spectrum (DMSO-*d*<sub>6</sub>, 100 MHz) of 2,3-

didemethyltetrahydropalmatine (11)



Figure S162. COSY spectrum of 2,3-didemethyltetrahydropalmatine (11) in DMSO-d<sub>6</sub>



Figure S163. HMQC spectrum of 2,3-didemethyltetrahydropalmatine (11) in DMSO-d<sub>6</sub>



Figure S164. HMBC spectrum of 2,3-didemethyltetrahydropalmatine (11) in DMSO-d<sub>6</sub>



Figure S165. NOESY spectrum of 2,3-didemethyltetrahydropalmatine (11) in DMSO-d<sub>6</sub>



Figure S166. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of stepholidine (12)



Figure S167. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD, 100 MHz) of stepholidine (12)



Figure S168. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of discretamine (13)





Figure S170. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of tetrahydropalmatine (14)



Figure S171. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of tetrahydropalmatine (14)



Figure S172. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of *N*-methylstepholidine (15)



Figure S173. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD, 100 MHz) of *N*-methylstepholidine (15)



Figure S174. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of cyclanoline (16)



**Figure S176.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub> + 5 drops CD<sub>3</sub>OD, 400 MHz) of *N*-methyltetrahydro-palmatine (17)



Figure S177. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub> + 5 drops CD<sub>3</sub>OD, 100 MHz) of N-

methyltetrahydro-palmatine (17)



Figure S178. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of jatrorrhizine (18)







Figure S182. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of dehydrocorydaline (20)



Figure S183. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of dehydrocorydaline (20)



Figure S184. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of pseudodehydrocorydaline (21)



Figure S185. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD, 100 MHz) of pseudodehydrocorydaline (21)



Figure S186. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of roemerine (22)



Figure S188. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of (-)-stephanine (23)





Figure S190. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of (-)-isolaureline (24)



Figure S191. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of (-)-isolaureline (24)



Figure S192. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of crebanine (25)



Figure S194. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub> + 5 drops CD<sub>3</sub>OD, 400 MHz) of dicentrine (26)



Figure S195. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub> + 5 drops CD<sub>3</sub>OD, 100 MHz) of dicentrine (26)



Figure S196. <sup>1</sup>H NMR sectrum (CDCl<sub>3</sub>, 400 MHz) of (-)-ushinsunine (27)



Figure S197. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of (-)-ushinsunine (27)



Figure S198. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of (-)-ayuthianine (28)


Figure S200. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of sukhodianine (29)



Figure S201. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of sukhodianine (29)



Figure S202. <sup>1</sup>H NMR spectrum (Acetone-*d*<sub>6</sub>, 400 MHz) of (–)-*N*-fonnylanonaine (30)



Figure S203. <sup>13</sup>C NMR spectrum (Acetone-*d*<sub>6</sub>, 100 MHz) of (–)-*N*-fonnylanonaine (30)



Figure S204. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of (-)-*N*-methylasimilobine (31)



Figure S205. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD, 100 MHz) of (-)-*N*-methylasimilobine (31)



Figure S206. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of (-)-asimilobine (32)



Figure S207. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD, 100 MHz) of (-)-asimilobine (32)



Figure S208. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of (-)-asimilobine-2-O-β-D-

glucoside (33)



Figure S209. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD, 100 MHz) of (–)-asimilobine-2-O-β-D-



Figure S210. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of lanuginosine (34)



Figure S212. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub> + 5 drops CD<sub>3</sub>OD, 400 MHz) of dicentrinone (35)



Figure S213. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub> + 5 drops CD<sub>3</sub>OD, 100 MHz) of dicentrinone (35)



Figure S214. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of oxocrebanine (36)



Figure S216. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of 8-methoxyuvoriopsine (37)



Figure S217. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of 8-methoxyuvoriopsine (37)



Figure S218. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of dehydroroemerine (38)



Figure S219. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of dehydroroemerine (38)



Figure S220. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of dehydrostephanine (39)



Figure S221. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of dehydrostephanine (39)



Figure S222. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of dehydroisolaureline (40)



Figure S223. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of dehydroisolaureline (40)



Figure S224. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of dehydrocrebanine (41)



Figure S226. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of dehydrodicentrine (42)



Figure S227. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of dehydrodicentrine (42)



Figure S228. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of (–)-crebanine-β-N-oxide (43)



Figure S229. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of (–)-crebanine-β-N-oxide (43)



Figure S230. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD, 400 MHz) of coclaurine (44)



Figure S231. <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD, 100 MHz) of coclaurine (44)



Figure S232. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz) of salutaridine (45)



Figure S233. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, 100 MHz) of salutaridine (45)



Figure S234. ECD spectra of stephapierrines A-D (1-4).



Figure S235. ECD spectra of stephapierrines E-F (5-6) and *O*,*N*-diacetylasimilobine (9).

	$ \begin{array}{c} 0 & 2 & 3 & 3a & 4 \\ 0 & 1 & 1b & 6a & N \\ 11 & 11a & 7 & H & CH_3 \\ 11 & 7a & H & CH_3 \\ 10 & 9 & 8 & 8 \\ \end{array} $ 22	о – – – – – – – – – – – – – – – – – – –	O O O O H CH <sub>3</sub> CH <sub>3</sub> 24	O O H CH <sub>3</sub> O CH <sub>3</sub> 25	о н <sub>3</sub> со ОСН <sub>3</sub> 26	<sup>0</sup> <sup>N</sup> <sup>H</sup> <sup>N</sup> <sup>H</sup> <sup>O</sup> <sup>N</sup> <sup>H</sup> <sup>O</sup> <sup>N</sup> <sup>H</sup> <sup>O</sup> <sup>N</sup> <sup>H</sup> <sup>O</sup> <sup>N</sup> <sup>H</sup> <sup>O</sup> <sup>N</sup> <sup>H</sup> <sup>O</sup> <sup>N</sup> <sup>H</sup> <sup>O</sup> <sup>N</sup> <sup>O</sup> <sup>N</sup> <sup>H</sup> <sup>O</sup> <sup>N</sup> <sup>N</sup> <sup>H</sup> <sup>O</sup> <sup>N</sup> <sup>N</sup> <sup>N</sup> <sup>N</sup> <sup>N</sup> <sup>N</sup> <sup>N</sup> <sup>N</sup>	HO H <sub>3</sub> CO H <sup>N</sup> H H <sup>3</sup> H
AChE <sup>a</sup>	$8.32\pm0.12$	$11.34\pm0.20$	$11.94\pm0.39$	$17.37\pm0.22$	6.11 ± 0.38	$140.15{\pm}~0.83$	$141.47\pm0.82$
BuChE <sup>a</sup>	$2.85\pm0.08$	$2.80\pm0.07$	$16.58\pm0.54$	$10.51\pm0.27$	$26.41\pm0.43$	inactive <sup>b</sup>	$10.08\pm0.15$
	о о н СН <sub>3</sub> У ОН 27	о о С С Н С Н <sub>3</sub> С Н <sub>3</sub> С Н С С Н С С Н С С Н С С Н С С Н С С Н С С С Н С С С С С Н С С С С С С С С С С С С С		CH <sub>3</sub> 29			
AChE <sup>a</sup>	$17.63\pm0.67$	$6.12 \pm 0.63$		$4.30\pm0.28$			
BuChE <sup>a</sup>	$7.42\pm0.16$	$5.87\pm0.06$		$22.47\pm0.10$			
	о с с с с с н <sub>3</sub> С н <sub>3</sub> С н <sub>3</sub>	от СН <sub>3</sub> ОСН <sub>3</sub> 39	он сна осна осна <b>40</b>	O O O O CH <sub>3</sub> CH <sub>3</sub> O CH <sub>3</sub> O CH <sub>3</sub> A A A A A A A A A A A A A	онности н <sub>3</sub> сонсн <sub>3</sub> 42		
AChEª	$1.21 \pm 0.09$	$2.85 \pm 0.24$	$147.18 \pm 0.71$	$32.49 \pm 0.52$	$1.09 \pm 0.02$		
BuChE <sup>a</sup>	$3.34\pm0.02$	$3.26\pm0.05$	$20.32\pm0.39$	$14.11\pm0.25$	$5.57\pm0.15$		

<sup>a</sup> IC<sub>50</sub> in μM <sup>b</sup> Inactive at 0.1 mg/ml



<sup>a</sup> IC<sub>50</sub> in μM <sup>b</sup> Inactive at 0.1 mg/ml