Anti-inflammatory alkaloid Glycoside and Quinoline alkaloid derivates from the stems of *Clausena lansium*

Jie Liu,^{*a*} Chuang-Jun Li,^{*a*} Lin Ni,^{*a*} Jing-Zhi Yang,^{*a*} Li Li,^{*a*} Cai-xia Zang,^{*a*} Xiu-Qi Bao,^{*a*} Dan Zhang,^{*a*} Dong-Ming Zhang^{**a*}

^a State Key Laboratory of Bioactive Substance and Function of Natural Medicines, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050, People's Republic of China E-mail: zhangdm@imm.ac.cn; Tel/fax: +86-10-63165227.

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Figure S1. The ¹H NMR (400 MHz) spectrum of Clausenaside A (1) in DMSO-d₆



Figure S2. The ¹³C NMR (100 MHz) spectrum of Clausenaside A (1) in DMSO-d₆





Figure S3. The DEPT spectrum of Clausenaside A (1) in DMSO-d₆





Figure S5. The HMBC spectrum of Clausenaside A (1) in DMSO-d₆



1.1 F2 (ppm) 2-3-5-7-8-. . F1 (ppm)

Figure S6. The ¹H-¹H COSY spectrum of Clausenaside A (1) in DMSO-*d*₆

Figure S7. The experimental CD spectrum of Clausenaside A (1)





Figure S8. The IR spectrum of Clausenaside A (1)

Figure S9. The HRESIMS of Clausenaside A (1)

MS Formula Results: + Scan (5.735 min)	Sub (2014011001.d)

		m/z	Ion	Formula	Abundance											
- 🗆		456.1634	(M+Na)+	C22 H27 N Na O8	499566.3											
		Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
		2	C22 H27 N O8	C22 H27 N Na O8	456.1629	99.97		433.1741	433.1737	-1.09	1.09	99.99	99.94	99.96	456.1634	10
		Г	C23 H23 N5 O4	C23 H23 N5 Na O4	456.1642	99.79		433.1741	433.175	1.98	1.98	99.48	99.99	99.88	456.1634	15
	П	۳	C23 H31 N O3 S2	C23 H31 N Na O3 S2	456.1638	97.45		433.1741	433.1745	0.9	0.9	91.52	99.52	99.98	456.1634	9
•	\Box	Г	C14 H31 N3 O10 S	C14 H31 N3 Na O10 S	456.1622	97.41		433.1741	433.173	-2.61	2.61	91.57	99.65	99.79	456.1634	1





Figure S11. The ¹³C NMR (150 MHz) spectrum of (S)-(+)-tembamide (1a) in DMSO- d_6



Figure S12. The experimental CD spectrum of (S)-(+)-tembamide (1a)



Figure S13. The HRESIMS of (S)-(+)-tembamide (1a)

MS Formula Results: + Scan (5.910 min) Sub (2015010601.d)

п	vz 🛛	lon	Formula	Abundance										
	294.1109	(M+Na)+	C16 H17 N Na O3	792599.5	1									
	Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
	~	C16 H17 N O3	C16 H17 N Na O3	99.85		271.1217	271.1208	294.1101	-3.05	3.05	99.76	99.94	99.94	9
	67	C13 H18 F N O4	C13 H18 F N Na O4	99.43		271.1217	271.122	294.1112	1.17	1.17	99.96	98.11	99.94	5
T	17	C13 H22 F N S Si	C13 H22 F N Na S Si	97.39		271.1217	271.1226	294.1118	3.5	3.5	99.68	91.75	99.59	4

Figure S14. The ¹H NMR (600 MHz) spectrum of (S)-MTPA-ester (1aa) in DMSO- d_6



Figure S15. The ¹³C NMR (150 MHz) spectrum of (S)-MTPA-ester (1aa) in DMSO- d_6





Figure S16. The HSQC spectrum of (S)-MTPA-ester (1aa) in DMSO-d₆



Figure S17. The HMBC spectrum of (S)-MTPA-ester (1aa) in DMSO-d₆

Figure S18. The ¹H NMR (600 MHz) spectrum of (*R*)-MTPA-ester (1ab) in DMSO- d_6



Figure S19. The ¹³C NMR (150 MHz) spectrum of (*R*)-MTPA-ester (1ab) in DMSO- d_6



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)



Figure S20. The HSQC spectrum of (*R*)-MTPA-ester (1ab) in DMSO-*d*₆



Figure S21. The HMBC spectrum of (R)-MTPA-ester (1ab) in DMSO-d₆

Figure S22. The ¹H NMR (400 MHz) spectrum of Clausenaside B (2) in DMSO-

*d*₆



Figure S23. The ¹³C NMR (100 MHz) spectrum of Clausenaside B (2) in DMSO- d_6





Figure S24. The DEPT spectrum of Clausenaside B (2) in DMSO-d₆

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

F2 (ppm) ø 2.5 000 3.0-~ Juril II ø 0 3.5 D ۵ 0 4.0 4.5 H 0 5.0 5.5-6.0-6.5-۰ 7.0 8 3 7.5 0 8.0 40 50 80 70 60 110 100 90 130 120 140 F1 (ppm)

Figure S25. The HSQC spectrum of Clausenaside B (2) in DMSO-d₆

Figure S26. The HMBC spectrum of Clausenaside B (2) in DMSO-d₆



ıll ku d F2 (ppm) . 2-7-F1 (ppm)

Figure S27. The ¹H-¹H COSY spectrum of Clausenaside B (2) in DMSO-d₆





Figure S29. The IR spectrum of Clausenaside B (2)



Figure S30. The HRESIMS of Clausenaside B (2)

MS Formula Results: + Scan (5.615 min) Su	b (2014121501.d)
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	m/z	lon	Formula	Abundance	6									
· 🗆	456.1635	(M+Na)+	C22 H27 N Na O8	1592229.4	1									
-	Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
		C22 H27 N O8	C22 H27 N Na O8	99.93		433.1743	433.1737	456.1629	-1.5	1.5	99.93	99.9	99.97	10
	Г	C19 H28 F N O9	C19 H28 F N Na O9	99.49		433.1743	433.1748	456.164	1.14	1.14	99.96	98.31	99.97	6
	Г	C21 H28 N3 O5 P	C21 H28 N3 Na O5 P	99.49		433.1743	433.1767	456.1659	5.4	5.4	99.11	99.74	99.93	10
	F	C22 H29 F N3 O P S	C22 H29 F N3 Na O P S	99.43		433.1743	433.1753	456.1645	2.26	2.26	99.84	98.66	99.54	10
	F	C21 H29 F N3 O2 P Si	C21 H29 F N3 Na O2 P Si	99.4		433.1743	433.1751	456.1643	1.71	1.71	99.91	98.43	99.56	10
	F	C25 H28 N3 P S	C25 H28 N3 Na P S	99.32		433.1743	433.1742	456.1634	-0.38	0.38	100	97.93	99.61	14
	-	C25 H25 F N3 O P	C25 H25 F N3 Na O P	99.3		433.1743	433.1719	456.1611	-5.52	5.52	99.08	99.16	99.93	15
	F	C23 H28 F N O4 S	C23 H28 F N Na O4 S	99.05		433.1743	433.1723	456.1615	-4.64	4.64	99.35	98.08	99.64	10
	- F	C18 H31 N O9 Si	C18 H31 N Na O9 Si	98.95		433.1743	433.1768	456.166	5.72	5.72	99.01	98.31	99.59	5
	F	C22 H28 F N O5 Si	C22 H28 F N Na O5 Si	98.9		433.1743	433.1721	456.1613	-5.19	5.19	99.18	97.81	99.65	10
	Г	C24 H28 N3 O P Si	C24 H28 N3 Na O P Si	98.82		433.1743	433.1739	456.1631	-0.93	0.93	99.97	96.21	99.63	14
	F	C13 H31 N3 O11 Si	C13 H31 N3 Na O11 Si	98.46		433.1743	433.1728	456.162	-3.58	3.58	99.61	95.78	99.38	1
	Г	C19 H32 F N O5 S Si	C19 H32 F N Na O5 S Si	97.87		433.1743	433.1754	456.1647	2.58	2.58	99.8	93.48	99.28	5
	r -	C22 H31 N O4 S Si	C22 H31 N Na O4 S Si	97.74		433.1743	433.1743	456.1635	-0.05	0.05	100	92.61	99.36	9
	Г	C23 H31 N O3 S2	C23 H31 N Na O3 S2	97.59		433.1743	433.1745	456.1638	0.5	0.5	99.99	92.1	99.36	9
	Г	C20 H32 F N O4 S2	C20 H32 F N Na O4 S2	97.22		433.1743	433.1757	456.1649	3.13	3.13	99.7	91.38	99.29	5
	_	C15 H36 N O7 P S Si	C15 H36 N Na O7 P S Si	97.1		433.1743	433.1719	456.1612	-5.53	5.53	99.07	92.09	99.16	0
	F	C14 H31 N3 O10 S	C14 H31 N3 Na O10 S	97.03		433.1743	433.173	456.1622	-3.02	3.02	99.72	90.53	99.44	1





Figure S32. The ¹³C NMR (100 MHz) spectrum of Clausenaside C (3) in DMSO- d_6





Figure S33. The DEPT spectrum of Clausenaside C (3) in DMSO- d_6
Figure S34. The HSQC spectrum of Clausenaside C (3) in DMSO-d₆



Figure S35. The HMBC spectrum of Clausenaside C (3) in DMSO-d₆



Figure S36. The ¹H-¹H COSY spectrum of Clausenaside C (3) in DMSO-*d*₆



Figure S37. The experimental CD spectrum of Clausenaside C (3)



Figure S38. The IR spectrum of Clausenaside C (3)



Figure S39. The HRESIMS of Clausenaside C (3)

	m/z	lon	Formula	Abundance											
	404.171	(M+H)+	C21 H26 N 07	771528.8											
1	Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	miz	DBE
- 1	2	C21 H25 N 07	C21 H26 N O7	404.1704	99.91		403.1637	403.1631	-1.46	1.46	99.96	99.81	99.93	404.171	10
.1	F	C22 H21 N5 03	C22 H22 N5 O3	404.1717	99.67		403.1637	403.1644	1.84	1.84	99.1	99.92	99.89	404.171	15
	P**	C19 H23 N4 O6	C19 H24 N4 O6	404.169	99.55		403.1637	403.1618	-4.8	4.8	99.91	99.91	99.24	404.171	10.5
	E	C24 H23 N2 O4	C24 H24 N2 O4	404.1731	99.12		403.1637	403.1658	5.18	5.18	98.51	99.83	99.12	404.171	14.5
. 1	F	C16 H27 N4 O6 S	C16 H28 N4 O5 S	404.1724	98.79		403.1637	403.1651	3.55	3.55	96.75	99.62	99.59	404.171	5.5
	17	C15 H31 O10 S	C15 H32 O10 S	404.1711	98.09		403.1637	403.1638	0.25	0.25	93.69	99.55	100	404.171	0.5
	E	C20 H27 N4 O S2	C20 H28 N4 O S2	404.1699	97.68		403.1637	403.1626	-2.65	2.65	92.73	99.43	99.77	404.171	9.5
	E	C13 H29 N3 O9 S	C13 H30 N3 O9 S	404.1697	97.62		403.1637	403.1625	-3.1	3.1	92 52	99.6	99.68	404.171	
	r l	C22 H29 N C2 S2	C22 H30 N O2 S2	404.1712	97.59		403.1637	403.164	0.68	0.68	92.07	99.44	99.98	404.171	\$
È	miz	lon	Formula	Abundance											
	426.1524	(M+Na)+	G21 H25 N Na 07	1251080.3											
1	Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
	2	C21 H25 N 07	C21 H25 N Na 07	426.1523	99.94	1	403.1632	403.1631	-0.18	0.18	99.83	99.97	100	428.1524	10
	E	C22 H21 N5 03	C22 H21 N5 Na 03	426.1537	99.8	8	403.1632	403.1644	3.12	3.12	99.85	99.93	99.71	426.1524	11
	C	C19 H23 N4 O6	C19 H23 N4 Na O5	426.151	99.64	1	403.1632	403.1618	-3.52	3.52	99.41	99.95	99.63	426.1524	10.5
	r i	C16 H27 N4 O6 S	C16 H27 N4 Na C6 S	426.1544	98.15	5	403.1632	403.1651	4.83	4.83	94.97	99.67	99.3	426.1524	5.1
	E	C20 H27 N4 O S2	C20 H27 N4 Na O S2	426.1518	97.61		403.1632	403.1626	-1.38	1.38	92.15	99.5	99.94	425.1524	9.5
	Г	C22 H29 N O2 S2	C22 H29 N Na O2 S2	426.1532	97.5	5	403.1632	403.164	1.96	1.96	91.75	99.61	99.88	426.1524	
. 1	r -	C15 H31 O10 B	C15 H31 Na O10 S	426.153	97.37	7	403.1632	403.1638	1.53	1.53	91.11	99.77	99.93	426.1524	0.5

MS Formula Results: + Scan (5.566 min) Sub (2014031201.d)



Figure S40. The ¹H NMR (600 MHz) spectrum of Clausenaside D (4) in DMSO- d_6





Figure S42. The DEPT spectrum of Clausenaside D (4) in DMSO-d₆



Figure S43. The HSQC spectrum of Clausenaside D (4) in DMSO-d₆



Figure S44. The HMBC spectrum of Clausenaside D (4) in DMSO-d₆



Figure S45. The ¹H-¹H COSY spectrum of Clausenaside D (4) in DMSO-d₆

110 105 90 95 85 80 75 70 65 55 50 45 30 25 20 15 10 55 998.9 M 718.5 947.8 539.7 W %Transmittance 680.0 0.768 2930.4 841.2 1022.5 -----1317.5 1163.6 623.8 450 992.5 1424.0 755.9 1383.9 1245.3 1615.5 3362.8 1080.7 3273.8 3501. 1640.6 0 -5 -10 4000 1500 Wavenumbers (cm-1) 3000 2000 1000 600 800 . .. 1.

Figure S46. The IR spectrum of Clausenaside D (4)

Figure S47. The HRESIMS of Clausenaside D (4)



MS Formula Results: + Scan (4.227 min) Sub (2014051402.d)



Figure S48. The ¹H NMR (600 MHz) spectrum of Clausenaside E (5) in DMSO-

*d*₆

Figure S49. The $^{13}\mathrm{C}$ NMR (150 MHz) spectrum of Clausenaside E (5) in DMSO- d_6





Figure S50. The DEPT spectrum of Clausenaside E (5) in DMSO-d₆

Figure S51. The HSQC spectrum of Clausenaside E (5) in DMSO-*d*₆



Figure S52. The HMBC spectrum of Clausenaside E (5) in DMSO-*d*₆



Figure S53. The ¹H-¹H COSY spectrum of Clausenaside E (5) in DMSO-*d*₆



Figure S54. The IR spectrum of Clausenaside E (5)



Figure S55. The HRESIMS of Clausenaside E (5)

	m/z	lon	Formula	Abundance							
	368.1346	(M+H)+	C17 H22 N O8	889722.2							
Г	Best	Formula (M)	Ion Formula	Score	Cross Score	Calc m/z	Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
· [~	C17 H21 N O8	C17 H22 N O8	99.9		368.134	-1.68	99.91	99.84	99.95	8
· [17	C14 H22 F N O9	C14 H23 F N O9	99.34		368.1351	1.43	99.93	97.86	99.95	4
· [5	C16 H23 F N3 O2 P Si	C16 H24 F N3 O2 P Si	99.31		368.1354	2.11	99.86	98.08	99.7	8
۰Ľ		C19 H22 N3 O P Si	C19 H23 N3 O P Si	98.6		368.1343	-1	99.97	95.34	99.77	12
	m/z	Ion	Formula	Abundance	1						
	390.1161	(M+Na)+	C17 H21 N Na O8	471258.3							
Γ	Best	Formula (M)	Ion Formula	Score	Cross Score	Calc m/z	Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
• [~	C17 H21 N O8	C17 H21 N Na O8	99.96		390.1159	-0.36	100	99.87	99.99	1
		C14 H22 F N O9	C14 H22 F N Na O9	99.69		390.1171	2.75	99.78	99.28	100	
+	- C -	C20 H19 F N3 O P	C20 H19 F N3 Na O P	98.88		390.1142	-5.1	99.24	97.35	99.99	13
•	F	C16 H23 F N3 O2 P Si	C16 H23 F N3 Na O2 P Si	98.81		390.1173	3.44	99.66	96.69	99.68	1
+	F	C17 H22 F N 05 Si	C17 H22 F N Na O5 Si	98.47		390.1143	-4.7	99.36	95.9	99.78	1
. [172 - C	C19 H22 N3 O P Si	C19 H22 N3 Na O P Si	97.91		390.1162	0.33	100	92.89	99.75	1:

MS Formula Results: + Scan (5.158 min) Sub (2014090101.d)





Figure S58. The HSQC spectrum of Clausenaside F (6) in MeOH-d₄



11 F2 (ppm) 3-JUL 4 5-6 7-8 9-170 160 150 140 130 120 90 50 100 80 70 60 110 F1 (ppm)

Figure S59. The HMBC spectrum of Clausenaside F (6) in MeOH-d₄



Figure S60. The ¹H-¹H COSY spectrum of Clausenaside F (6) in MeOH-*d*₄

Figure S61. The IR spectrum of Clausenaside F (6)



Figure S62. The HRESIMS of Clausenaside F (6)

MS Formula Results: + Scan (5.404 min) Sub (2014031202.d)

míz	kan	Formula	Abundance											
378.118	(M+H)+	C18 H20 N O8	398447.1											
Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
	C18 H19 N O8	C18 H20 N O5	378.1183	99.97		377.1107	377.1111	0.85	0.85	99.93	100	99.98	378.118	10
Г	C16 H17 N4 O7	C16 H18 N4 O7	378.117	99.77		377.1107	377.1097	-2.72	2.72	99.62	29.98	99.76	378.118	10.5
F	C19 H15 N5 O4	C19 H16 N5 O4	378.1197	99.61		377.1107	377.1124	4.39	4.39	99.68	99.98	99.38	378.118	15
F	C22 H19 N O3 S	C22 H20 N C3 S	378.1158	98.42		377.1107	337.1086	-5.79	5.79	96.51	99.73	98.92	378.118	14
F	C25 H17 N2 S	C25 H18 N2 S	378.1185	98.13		377.1107	377.1112	1.32	1.32	93.76	99.76	99.94	378.118	18.5
Г	C17 H21 N4 02 52	C17 H22 N4 O2 S2	378.1179	97.46		377.1108	377.1106	-0.42	0.42	91.66	99.36	99.99	378.118	9.5
F	C12 H25 O11 S	C12 H26 O11 S	378.119	97.21		377.1107	377.1118	2.68	2.68	90.91	99.64	99.77	378.118	0.5
-	C19 H23 N O3 S2	C19 H24 N 03 S2	378.1192	97.2		377.1107	377.1119	3.15	3.15	91.19	99.45	99.68	378.118	5
m/z	lon	Formula	Abundance											
m/z 400.0999	lon (M+Na)+	Formula C18 H19 N Na C8	Abundance 244096.8											
m/z 400.0999 Best	lon (M+Na)+ Formula (M)	Formula C18 H19 N Na O8 Ion Formula	Abundance 244096.8 Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	míz	DBE
m/z 400.0999 Best	lon (M+Na)+ Formula (M) C18 H19 N OB	Formula C18 H19 N Na O6 Ion Formula C18 H19 N Na O8	Abundance 244096.8 Calc m/z 400.1003	Score 99.95	Cross S	Mass 377.1107	Calc Mass 377.1111	Diff (ppm) 0.95	Abs Diff (ppm) 0.96	Abund Malch 99.92	Spacing Mat 99.95	Mass Match 99.97	m/z 400.0959	DBE 10
m'z 400.0999 Beist	lon (M+Na)+ Formula (M) C18 H19 N O8 C16 H17 N4 O7	Formula C18 H19 N Na C6 Ion Formula C18 H19 N Na C8 C16 H17 N4 Na C7	Abundance 244096.8 Calc m/z 400.1003 400.0989	Score 99.95 99.8	Cross S	Mass 377.1107 377.1107	Calc Mass 377.1111 377.1097	Diff (ppm) 0.96 -2.61	Abs Diff (ppm) 0.96 2.61	Abund Match 99.92 99.52	Spacing Mat 99.95 100	Mass Match 99.97 99.8	m/z 400.0999 400.0999	DBE 10 10.5
m/z 400.0999 Best 9	lon (M+Na)+ Formula (M) C18 H19 N O8 C16 H17 N4 O7 C19 H15 N5 O4	Formula C18 H19 N Na O8 Ion Formula C16 H19 N Na O8 C16 H17 N4 Na O7 C19 H15 N5 Na O4	Abundance 244096.8 Calc m/z 400.1003 400.0989 400.1016	Score 99.95 99.8 99.52	Cross S	Mass 377.1107 377.1107 377.1107	Calc Mass 377.1111 377.1097 377.1124	Diff (ppm) 0.98 -2.61 4.5	Abs Diff (ppm) 0.96 2.61 4.5	Abund Match 99.92 99.62 99.32	Spacing Mat 99.95 100 100	Mass Malch 99.97 99.8 99.41	m/z 400.0999 400.0999 400.0999	DBE 10 10.5 15
m/z 400.0999 Best 7	Ion (M+Na)+ Formule (M) C16 H19 N OB C16 H17 N4 O7 C19 H15 N5 O4 C22 H19 N O3 S	Formula C18 H19 N Na O8 Ion Formula C16 H19 N Na O8 C16 H17 N4 Na O7 C19 H15 N5 Na O4 C22 H19 N No O3 S	Abundance 244096.8 Colic m/z 400.1003 400.0989 400.1016 400.0978	Score 99.95 99.8 99.52 98.63	Cross S	Mass 377.1107 377.1107 377.1107 377.1107 377.1107	Calc Mass 377.1111 377.1097 377.1124 377.1086	Diff (ppm) 0.96 -2.61 4.5 -5.68	Abs Diff (ppm) 0.96 2.61 4.5 5.68	Abund Match 99.92 99.62 99.32 97.07	Spacing Mat 99.95 100 100 99.65	Mass Match 99.97 99.8 99.41 99.06	m/2 400.0999 400.0999 400.0999 400.0999	DBE 10 10.5 15 14
m/z 400.0999	Ion (M+Na)+ Formula (M) C18 H19 N OB C19 H15 N5 G4 C22 H19 N O3 C25 H17 N2 S	Formula C18 H19 N Na OB C18 H19 N Na OB C18 H19 N Na OB C16 H17 N4 Na O7 C19 H15 N5 Na O4 C22 H19 N Na O35 C25 H17 N2 Na S	Abundance 244096.8 Calc m/z 400.1003 400.0989 400.1016 400.0978 400.1005	Score 99.95 99.8 99.52 98.63 98.2	Cross S	Mass 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107	Calc Mass 377.1111 377.1097 377.1124 377.1086 377.112	Diff (ppm) 0.96 -2.61 4.5 -5.68 1.43	Abs Diff (ppm) 0.96 2.61 4.5 5.68 1.43	Abund Match 99.92 99.62 99.32 97.07 94.03	Spacing Mat 99.95 100 100 99.65 99.71	Mass Match 99.97 99.8 99.41 99.05 99.04	m/z 400.0999 400.0999 400.0999 400.0999 400.0999	DBE 10 10.1 15 14 18.5
m/z 400.0999 Best F	Ion (M+Na)+ Formula (M) C18 H19 N DB C18 H19 N DB C19 H17 N 03 S C22 H19 N 03 S C25 H17 N 2 S C17 H21 H2 Q S	Fernula C18 H19 N Na OB Ion Fernula C18 H19 N Na OB C18 H17 NA Na OT C19 H15 NS Na OA C22 H19 N Na O3 S C25 H17 N2 Na S C17 H21 N4 Na O2 S2	Abundance 244098.8 Calc m/z 400.1003 400.0989 400.1016 400.0978 400.1005 400.0996	Score 99.95 99.8 99.52 98.63 98.2 98.2 97.91	Cross S	Mass 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107	Calc Mass 377.1111 377.1097 377.1124 377.1086 377.1112 377.1106	Diff (pprr) 0.96 -2.61 4.5 -5.68 1.43 -0.31	Abs Diff (ppm) 0.96 2.61 4.5 5.68 1.43 0.31	Abund Match 99 92 99 62 99 32 97 07 94 03 93 27	Spacing Mat 99.95 100 100 99.66 99.71 99.29	Mass Match 99.97 99.8 99.41 99.06 99.94 100	m/z 400.0999 400.0999 400.0999 400.0999 400.0999 400.0999	DBE 10 10.1 15 14 18.5 9.5
m/z 400.0999 Best C C C C C C C C C C C C C C C C C C C	100 (M+Na)+ Formula (M) C18 H19 N OB C18 H19 N OB C19 H15 N5 O4 C25 H17 N2 S C17 H21 N4 O2 S2 C17 H21 N4 O2 S2 C19 H23 N O3 S2	Fernula C18 H19 N Na OB C18 H19 N Na OB C18 H19 N Na OB C18 H17 N Na OS C22 H19 N Na O3 C22 H19 N Na O3 C27 H17 N2 Na O3 C17 H17 N4 Na O2 S2 C19 H20 Na O3 S3	Abundance 244098.8 Calc m/z 400.1003 400.0989 400.1016 400.0978 400.1005 400.9968 400.1012	Score 99.95 99.8 99.52 98.63 98.2 98.2 97.91 97.63	Cross S	Mass 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107	Caic Mass 377,1111 377,1097 377,1096 377,1108 377,1108 377,1109 377,1109	Diff (ppm) 0.96 -2.51 4.5 -5.58 1.43 -0.31 3.26	Abs Diff (ppm) 0.86 2.61 4.5 5.60 1.43 0.31 3.26	Abund Match 99 92 99 62 99 32 97 07 94 03 80 27 92 77	Spacing Mat 99.95 100 100 99.66 99.71 99.29 99.36	Mass Maich 99.97 99.8 99.41 99.06 99.94 100 99.69	m/2 400.0999 400.0999 400.0999 400.0999 400.0999 400.0999 400.0999	DBE 10 10 19 14 18 9 5
m/z 400.0999 Best F F F F F F F F F F F F F F F F F F F	ton (M+Na)+ Formate (M) C18 H19 N 08 C16 H17 N4 07 C18 H17 N4 07 C22 H19 N 03 S C37 H21 N4 02 S2 C19 H23 N 03 S2 C19 H23 N 03 S2 C12 H25 O13 S	Female C18 H19 N Na C8 Ion Ferma C18 H17 N Na C8 C18 H17 N Na C9 C22 H19 N No C3 C22 H19 N No C3 C22 H19 N No C3 C17 H21 N4 No C3 C17 H21 N4 No C3 C17 H23 NA C3 C17 H23 N	Abundance 244096.8 Calc m/r 400.1003 400.0959 400.1016 400.0978 400.1016 400.0966 400.0966 400.1012 400.1012	Score 99.95 99.8 99.52 98.63 98.2 97.91 97.63 97.63	Cross S	Mass 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107	Calc Mass 377.1111 377.1097 377.1124 377.1086 377.1105 377.1105 377.1109 377.1119	Diff (ppm) 0.98 -2.61 4.5 5.68 1.43 -0.31 3.26 2.79	Abs Diff (ppm) 0.96 2.61 4.5 5.68 1.43 0.31 0.31 0.32 6 2.79	Abund Match 99.92 99.62 99.32 97.07 94.03 98.27 92.27 92.24	Spacing Mat 99.95 100 100 99.66 99.71 99.29 99.36 99.55	Mass Malch 99.97 99.8 99.41 99.96 99.94 100 99.69 99.77	m/2 400.0999 400.0999 400.0999 400.0999 400.0999 400.0999 400.0999 400.0999	DBE 10 101 15 14 185 9 5 9 5 0 5
m/z 400.0999 Best F F F F F F F F F F F F F F F F F F F	100 (M+Na)+ Formule (M) C18 H19 N OB C16 H19 N OB C16 H17 NA 07 C22 H19 N 03 5 C25 H17 N2 5 C17 H2 N4 02 82 C19 H23 NA 015 C10 H23 NA 015 C10 H23 NA 015	Famula C18 H19 N Na OB C18 H19 N Na OB C18 H19 N Na OB C18 H17 M Na O C20 H17 NA Na OS C20 H17 NA Na OS C17 H1 M Na OS C17 H17 H Na OS C17 H21 NA Na OS C17 H21 NA Na OS C17 H25 Na OS C17 H25 Na OS	Abundance 244096.8 Celi: m/z 460.1003 400.0989 400.1016 400.0978 400.1016 400.0978 400.1016 400.0978 400.1016 400.0978	Score 99.95 99.8 99.52 96.63 98.2 97.91 97.93 97.53 97.52 97.27	Cross S	Mass 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107 377.1107	Calc Mass 377,1111 377,1097 377,1124 377,1086 377,1112 377,1108 377,1119 377,1119	Diff (ppm) 0.96 -2.51 4.5 -5.68 1.43 -0.31 -0.31 -0.326 2.79 -0.78	Abs Diff (ppm) 0.96 2.61 4.5 5.68 1.43 0.31 3.26 2.99 0.78	Abund Match 99.92 99.62 97.07 94.03 93.27 94.03 93.27 92.77 92.44 90.87	Specing Mat 99.95 100 100 99.66 99.79 99.29 99.36 99.55 99.52	Mass Match 99.97 99.8 99.41 99.06 99.94 100 99.69 99.69 99.59	m/z 400.0989 400.0989 400.0989 400.0989 400.0989 400.0989 400.0989 400.0989	DBE 10 10 15 14 18 5 95 9 5 9 0 5

Figure S63. The ¹H NMR (600 MHz) spectrum of Clausenaside G (7) in DMSO- d_6







Figure S65. The HSQC spectrum of Clausenaside G (7) in DMSO-*d*₆

Figure S66. The HMBC spectrum of Clausenaside G (7) in DMSO- d_6





Figure S67. The ¹H-¹H COSY spectrum of Clausenaside G (7) in DMSO-*d*₆

Figure S68. The IR spectrum of Clausenaside G (7)



Figure S69. The HRESIMS of Clausenaside G (7)

MS Formula Results: + Scan (6.414 min) Sub (2014110201.d)

E		m/z	lon	Formula	Abundance										
٠Ľ		282.1107	(M+Na)+	C15 H17 N Na O3	361227.5										
		Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
	•		C15 H17 N O3	C15 H17 N Na O3	98.24		259.1215	259.1208	282.1101	-2.49	2.49	99.84	97.03	96.49	8
Figure S70. Two conformations of Clausenaside G (7)



Figure S71. Calculated ECD spectra of 3S (7a), Calculated ECD spectra of 3R (7b) and experimental ECD spetrum of Clausenaside G (7)





Figure S73. The $^{13}\mathrm{C}$ NMR (100 MHz) spectrum of Clausenaside H (8) in DMSO- d_6





Figure S74. The DEPT spectrum of Clausenaside H (8) in DMSO-d₆

Figure S75. The HSQC spectrum of Clausenaside H (8) in DMSO-d₆





Figure S76. The HMBC spectrum of Clausenaside H (8) in DMSO-d₆



Figure S77. The ¹H-¹H COSY spectrum of Clausenaside H (8) in DMSO-*d*₆



Figure S78. The NOE difference spectrum of Clausenaside H (8) in DMSO-d₆



Figure S73. The IR spectrum of Clausenaside H (8)

Figure S74. The HRESIMS of Clausenaside H (8)

ſ	m/z		lo1	Formula	Abundance										
- [20	0.128	(M+H)+	C15 H18 N O3	425025.8										
	Best		Formula (M)	Ion Formula	Score	Cross Score	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
3			C15 H17 N O3	C15 H18 N O3	99.97		259.1207	259.1208	260.1281	0.53	0.53	99.99	99 93	99.96	8
ſ	m/z		Ion	Formula	Abundance										
٠C	28	1102	(M+Na)+	C15 H17 N Na O3	642807.4										
	Best		Formula (M)	Ion Formula	Score	Cross Score	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
			C15 H17 N O3	C15 H17 N Na O3	99.99		259.121	259.1208	282.1101	-0.42	0.42	100	99.99	99.97	8

MS Formula Results: + Scan (6.466 min) Sub (2014091103.d)