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SUPPORTING INFORMATION

Title: Calopins and Cyclocalopins – Bitter Principles from *Boletus calopus* and Related Mushrooms
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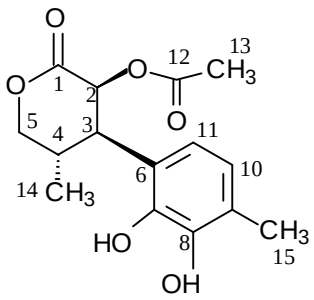
Ref. No.: O02137

The supporting information includes data on the NMR correlation signals from the HMBC and NOESY experiments of *O*-acetylcalopin (**1a**), *O*-acetylcyclocalopin A (**6a**) and of the cyclocalopins B (**7**), D (**10a**), E (**11**) and F (**12**).

O-Acetylcalopin



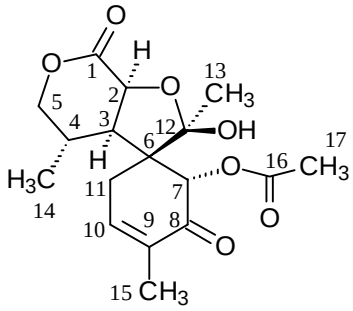
O-Acetylcalopin (**1a**)

Table 1. ^{1}H and ^{13}C NMR data of *O*-Acetylcalopin (**1a**), recorded in $CDCl_3$ at 600 MHz and 150.9 MHz.

					Proton correlation partner from 2D NMR	
Pos.	δ_C [ppm]	δ_H [ppm]		J_{HH} [Hz]	HMBC	NOESY
1	170.1					
2	67.7	5.66	d	9.3	C-1, C-6, C-12	3-H, 5α-H
3	45.6	3.60	dd	9.3, 9.3	C-1, C-4, C-7, C-11, C-14	2-H, 5α-H, 11-H, 14-CH_3
4	34.1	2.58	m			5β-H, 11–H
5α	71.7	4.15	dd	11.5, 11.5		2-H, 3-H
5β		4.35	dd	11.5, 4.4	C-1	4-H
6	122.1					
7	142.9					
8	142.0					
9	124.2					
10	121.8	6.60	d	7.8	C-6, C-8, C-15	11-H, 15-CH_3
11	122.4	6.49	d	7.8	C-7, C-9	3-H, 4-H, 10-H
12	169.9					
13	20.3	1.77	s		C-12	
14	15.8[a]	1.02	d	6.7	C-4, C-5	3-H
15	15.6[a]	2.22	s		C-8, C-9, C-10	10-H

[a]Assignments may be interchanged.

O-Acetylcyclocalopin A



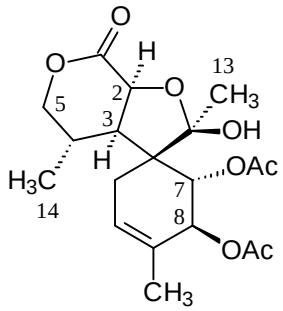
O-Acetylcyclocalopin A (**6a**)

Table 2. ^{1}H and ^{13}C NMR data of *O*-Acetylcyclocalopin A (**6a**), recorded in $CDCl_3$ at 600 MHz and 150.9 MHz.

					Proton correlation partner from 2D NMR	
Pos.	δ_C [ppm]	δ_H [ppm]		J_{HH} [Hz]	HMBC	NOESY
1	172.4					
2	73.7	4.65	d	10.5	C-1, C-12	3-H, 5α-H, 13-CH_3
3	47.4	2.43	dd	10.5, 10.5	C-1, C-4, C-6, C-7, C-12, C-14	2-H, 5α-H, 14-CH_3
4	30.8	2.28	m			11α-H
5α	72.2	3.86	dd	11.2, 11.2	C-4	2-H, 3-H
5β		4.10	dd	11.2, 3.5	C-1, C-3	11α-H
6	55.1					
7	77.2	5.47	s		C-3, C-6, C-12, C-16	11β-H, 13-CH_3
8	193.2					
9	134.3					
10	143.1	6.68	m		C-6, C-8	15-CH_3
11α	28.0	2.76	ddq	20.8, 4.3, 1.5	C-6	4-H, 5β-H
11β		2.58	dd	20.8, 2.6	C-6, C-7, C-15	7-H, 13-CH_3
12	107.2					
12-OH		2.67[a]	s, br.			
13	21.3	1.47	s		C-6, C-12	7-H, 11β-H
14	16.2	0.81	d	6.4	C-4	3-H
15	15.2	1.84	m		C-8, C-9, C-10	10-H
16	169.9					
17	20.8	2.21	s		C-16	

[a] δ_H depends on sample concentration.

Cyclocalopin B



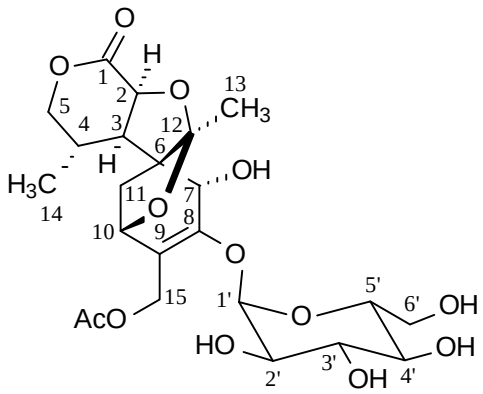
Cyclocalopin B (**7**)

Table 3. ^{1}H and ^{13}C NMR data of Cyclocalopin B (**7**), recorded in $CDCl_3$ at 600 MHz and 150.9 MHz.

					Proton correlation partner from 2D NMR	
Pos.	δ_C [ppm]	δ_H [ppm]		J_{HH} [Hz]	HMBC	NOESY
1	172.8					
2	73.9	4.61	d	10.6	C-1, C-3, C-4, C-6, C-12	3-H, 5α-H
3	48.1	2.69	dd	10.6, 10.6	C-1, C-2, C-4, C-6, C-7, C-12, C-14	2-H, 5α-H, 8-H, 14-CH_3
4	31.0	2.32	m			5β-H, 14-CH_3
5α	72.3	3.94	dd	11.1, 11.1	C-3, C-4	2-H, 3-H, 5β-H, 14-CH_3
5β		4.14	dd	11.1, 4.3	C-1, C-3, C-4, C-14	4-H, 5α-H, 14-CH_3
6	52.9					
7	74.0	5.27	d	8.7	C-3, C-6, C-8, C-12, 7-CH_3*C*OO	11β-H, 13-CH_3
8	73.5	5.56	s, br.			3-H, 14-CH_3, 15-CH_3, 8-C*H*$_3$COO
9	130.8					
10	124.6	5.56	s, br.			11α-H, 11β-H, 15-CH_3
11α	27.3	2.41	dm	19.9		10-H,11β-H, 14-CH_3
11β		2.20	dm	19.9		7-H, 10-H, 11α-H, 13-CH_3
12	108.3					
13	21.0	1.46	s		C-6, C-12	7-H, 11β-H
14	15.6	0.95	d	6.6	C-3, C-4, C-5	3-H, 4-H, 5α-H, 5β-H, 8-H, 11α-H
15	18.0	1.63	s, br.		C-9, C-10	8-H, 10-H
7-CH_3*C*OO	170.1					
7-*C*H$_3$COO	21.2	2.01	s		C-7[w], 7-CH_3*C*OO	
8-CH_3*C*OO	171.0					
8-*C*H$_3$COO	20.7	2.07	s		C-8[w], 8-CH_3*C*OO	8-H

[w] weak: Correlation signal of low intensity.

Cyclocalopin D

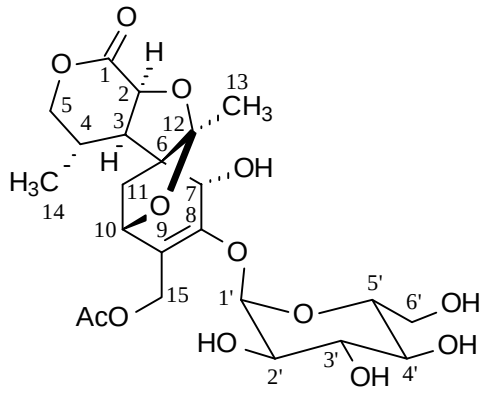


Cyclocalopin D (**10a**)

Table 4. ^{1}H and ^{13}C NMR data of Cyclocalopin D (**10a**), recorded in CD_3OD at 600 MHz and 150.9 MHz.

					Proton correlation partner from 2D NMR	
Pos.	δ_C [ppm]	δ_H [ppm]		J_{HH} [Hz]	HMBC[*]	NOESY[*]
1	176.0					
2	74.6	4.77	d	10.7	C-1, C-3, C-6, C-12	3-H, 5α-H, 13-CH_3[w], 14-CH_3[w]
3	50.7	2.81	dd	10.7	C-1, C-2, C-4, C-6, C-7, C-14	2-H, 7-H, 13-CH_3, 14-CH_3
4	32.4	2.05	m		C-3, C-14	5β-H, 14-CH_3
5α	72.6	4.03	dd	11.5, 11.5	C-3, C-4, C-14	2-H, 5β-H, 14-CH_3
5β		4.15	dd	11.5, 4.4	C-1, C-3, C-4, C-14	4-H, 5α-H, 14-CH_3
6	61.9					
7	69.4	4.40	s, br.		C-3, C-6, C-8, C-9, C-11	3-H, 13-CH_3
8	152.4					
9	118.6					
10	77.9	4.62	d	5.1	C-6, C-8, C-11, C-12	11β-H
11α	33.1	2.09	d	11.3	C-6, C-7, C-12	11β-H
11β		1.68	dd	11.3, 5.1	C-3, C-6, C-7, C-9, C-10	10-H, 11α-H
12	117.8					
13	24.4	1.35	s		C-6, C-7, C-12	2-H[w], 3-H, 7-H
14	17.2	1.26	d	6.6	C-3, C-4, C-5	2-H[w], 3-H, 4-H, 5α-H, 5β-H
15_a	61.1	4.70	d	12.3	C-8, C-9, C-10, 15-CH_3*C*OO	
15_b		4.80	d	12.3	C-7[w],C -8, C-9, C-10, 15-CH_3*C*OO	

Cyclocalopin D



Cyclocalopin D (**10a**)

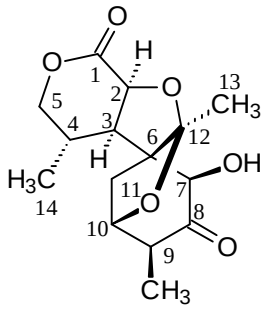
Table 4. ^{1}H and ^{13}C NMR data of Cyclocalopin D (**10a**), (cont.) recorded in CD_3OD at 600 MHz and 150.9 MHz.

					Proton correlation partner from 2D NMR	
Pos.	δ_C [ppm]	δ_H [ppm]		J_{HH} [Hz]	HMBC[*]	NOESY[*]
15-CH_3*C*OO	172.9					
15-*C*H_3COO	20.8	2.02	s		C-15, 15-CH_3*C*OO	
1'	97.0	5.75	d	3.5	C-8, C-5'	2'-H
2'	73.1	3.53	dd	9.3, 3.5	C-3', C-4'	1'-H
3'	74.6	3.78	dd	9.3, 9.3	C-2', C-4'	
4'	71.1	3.44	dd	9.3, 9.3	C-5', C-6'	
5'	75.0	3.72	m			
$6'_a$	62.0	3.73	m			
$6'_b$		3.75	m			

[*] From the hexose moiety only selected correlation signals are given.

[w] weak: correlation signal of low intensity

Cyclocalopin E



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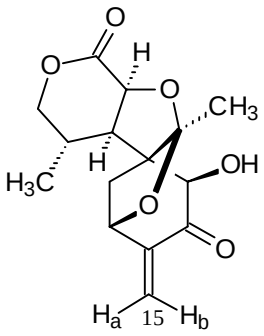
Cyclocalopin E (**11**)

Table 5. ^{1}H and ^{13}C NMR data of Cyclocalopin E (**11**), recorded in $CDCl_3$ at 600 MHz and 150.9 MHz.

					Proton correlation partner from 2D NMR	
Pos.	δ_C [ppm]	δ_H [ppm]		J_{HH} [Hz]	HMBC	NOESY
1	171.8					
2	71.0	4.50	d	11.2	C-1, C-3, C-6, C-12	3-H, 5α-H, 13-CH_3
3	43.0	3.09	dd	11.2, 10.6	C-1, C-2, C-4, C-6, C-7, C-11, C-14	2-H, 5α-H, 13-CH_3, 14-CH_3
4	32.0	2.05	m			5α-H, 5β-H
5α	71.7	3.96	dd	11.3, 11.2	C-1, C-3, C-4, C-14	2-H, 3-H, 4-H, 5β-H
5β		4.19	dd	11.2, 3.8	C-1, C-3, C-4, C-14	4-H, 5α-H
6	58.8					
7	76.2	4.29	s		C-6, C-8, C-10, C-11, C-12	9-H, 11α-H, 14-CH_3
7-OH		3.70	s, br.			
8	209.3					
9	50.6	2.49	m		C-8, C-15	7-H, 10-H, 11α-H
10	81.8	4.45	br. d	6.1	C-8, C-12, C-15	9-H, 11α-H, 11β-H, 15-CH_3
11α	37.4	1.89	d	12.2	C-6, C-7, C-9	7-H, 9-H, 10-H, 11β-H
11β		2.40	dd	12.2, 6.1	C-3, C-6, C-7, C-9, C-10	10-H, 11α-H
12	116.2					
13	21.6	1.26	s		C-6, C-12	2-H, 3-H
14	15.8	1.20	d	6.8	C-3, C-4, C-5	3-H, 7-H
15	11.2	1.25	d	7.0	C-8, C-9, C-10	10-H

Cyclocalopin F



Cyclocalopin F (**12**)

Table 6. ^{1}H and ^{13}C NMR data of Cyclocalopin F (**12**) as 1:3 admixture with **11,** recorded in $CDCl_3$ at 600 MHz and 150.9 MHz.

					Proton correlation partner from 2D NMR	
Pos.	δ_C [ppm]	δ_H [ppm]		J_{HH} [Hz]	HMBC	NOESY
1	171.8[a]					
2	71.5	4.56	d	11.4	C-1, C-3	3-H
3	43.1	3.18	dd	11.4, 10.0	C-2, C-4, C-6, C-14	2-H, 14-CH_3
4	31.9	2.06[a]	m			
5α	71.6	3.98	dd	11.4, 11.2	[a]	[a]
5β		4.20	dd	11.2[a]		[a]
6	58.8[a]					
7	76.5	4.25	s		C-6, C-8, C-11, C-12	11α-H, 14-CH_3
7-OH		3.59	s, br.			
8	199.6[b]					
9	144.7					
10	80.5	4.93	d	6.1	C-6, C-8, C-12, C-15	15_a-H
11α	36.9	1.84	d	12.3	C-6, C-7, C-12	7-H
11β		2.46	dd	12.3, 6.1	C-6, C-7, C-9, C-10	
12	116.2[a]					
13	22.9	1.38	s		C-6, C-12	
14	15.8	1.19	d	6.8		3-H, 7-H
15_a	122.2	5.42	s		C-8, C-10	10-H, 15_b-H
15_b		5.98			C-8, C-9, C-10	15_a-H

[a] overlapping with signals from **11**

[b] from HMBC experiment