Table S1. Viability of cell line after treatment with *H. rhodopensis* total extracts or fractions for 48 hours (%)

	MCF10A	MCF7	MDA-MB231
untreated	100±12	100±5.7	100±3.4
Total extract 10	109±10	109±6.7	96±3.9
Total extract 100	102±12	103±8.4	116±4.3
Total extract 200	86.3±3.3	105±8.9	76±8.6
Total extract 300	73±2	71±5.7	82±4.6
Fraction 7.	79±3.8	100±3	135±12
Fraction 8	78±9	100±2	99±3
Fraction 10	108±8	150±6	135±5
Fraction 11	94±4.8	100±9	110±1
Fraction 12	83±8.8	100±3	77±3.5
Fraction 13	84±8.7	78±2	70±2
Fraction 14	98±3.8	60.2±2.1	71±7.7
Fraction 15	79.8±9.1	84±3.7	71±4.4
Fraction 16	94±8.2	80±2.7	70.6±3.8
Fraction 17	86.6±10	65±4.8	77.7±1.4
Fraction 18	95.5±8.7	62±2.9	77.3±7.5

The concentration of total extract and fractions is in µg/ml. The fractions are applied in concentration 300 µg/ml. The standard errors of the means are presented in the table

Table S2. Metabolic content of fraction 14. On the first row is Myconoside (14% of total metabolic content).

Peak	RT	Area	% TIC
25	10.222	3768245905	13.78
31	11.702	1889734503	6.91
88	33.381	2675000438	3.56
50	16.786	2644637516	3.52
82	31.437	739519722.7	2.70
26	10.49	723044156.6	2.64
24	9.941	652300475.2	2.38
1	1.037	1630400747	2.17
80	30.274	571398912.9	2.09
29	11.237	509395070.9	1.86
16	8.264	491478268.5	1.80
47	15.158	460907523.2	1.69
28	10.839	449009787.9	1.64
32	12.167	444662824.8	1.63
34	12.466	426427765.5	1.56
6	4.061	412634324.8	1.51
76	29.195	376803650.8	1.38
86	32.517	349616097.6	1.28
5	3.38	344512627	1.26
36	12.865	341487606.2	1.25
33	12.317	338949427.7	1.24
81	30.955	337343692	1.23
48	15.573	333557899	1.22
87	32.999	332433994.7	1.22
66	23.297	328497428.2	1.20
84	31.985	325727459.2	1.19
22	9.543	315471340.8	1.15
30	11.287	312438307.1	1.14
83	31.62	309841415.2	1.13
35	12.583	297605710.9	1.09
75	28.979	286499505.1	1.05

74	28.115	263714892.8	0.96
54	18.33	246284064	0.90
85	32.384	244533347.1	0.89
55	18.812	237098521.1	0.87
56	19.095	212701327.5	0.78
89	33.995	211013200	0.77
12	7.383	210373707.1	0.77
78	29.676	207055140.3	0.76
21	9.31	204509134.7	0.75
44	14.36	195443560.1	0.71
79	30.042	184430601.3	0.67
45	14.51	184353713.2	0.67
77	29.361	179426221.7	0.66
23	9.659	176564480.3	0.65
39	13.447	175465559.2	0.64
37	13.031	173933505.3	0.64
51	17.134	170027038.6	0.62
13	7.549	163008705.4	0.60
2	1.453	161187318.9	0.59
14	7.782	141999158.8	0.52
57	19.643	135318378.3	0.49
20	9.111	130925307.6	0.48
3	2.084	130852615.1	0.48
27	10.706	128082626.8	0.47
73	27.533	126070148.4	0.46
19	8.978	125738003.9	0.46
15	8.081	117540147.9	0.43
18	8.762	113868015.3	0.42
10	5.174	109844551.7	0.40
17	8.579	109264731.8	0.40
7	4.26	108180114.5	0.40
59	20.34	106636914.6	0.39
72	27.101	105678965.1	0.39
41	13.812	97717757.39	0.36
38	13.247	96330702.41	0.35
69	24.66	95718211.95	0.35

62	21.437	92622127.89	0.34
71	26.769	88570761.84	0.32
9	4.675	87555865.7	0.32
67	23.53	86656917.03	0.32
58	20.025	81419122.77	0.30
42	14.094	78801693.78	0.29
40	13.613	78584143.18	0.29
61	20.889	77676851.18	0.28
43	14.178	68483492.13	0.25
49	16.254	67804658.17	0.25
63	21.968	66453737.03	0.24
8	4.46	64611207.42	0.24
64	22.135	61170472.08	0.22
68	24.344	59328787.11	0.22
53	18.065	52867561.25	0.19
4	3.097	52647372.23	0.19
11	6.37	46825708.06	0.17
70	24.975	46450943.23	0.17
60	20.59	44763314.28	0.16
52	17.815	41561180.11	0.15
65	22.5	41121646.11	0.15
46	14.859	39519131.09	0.14

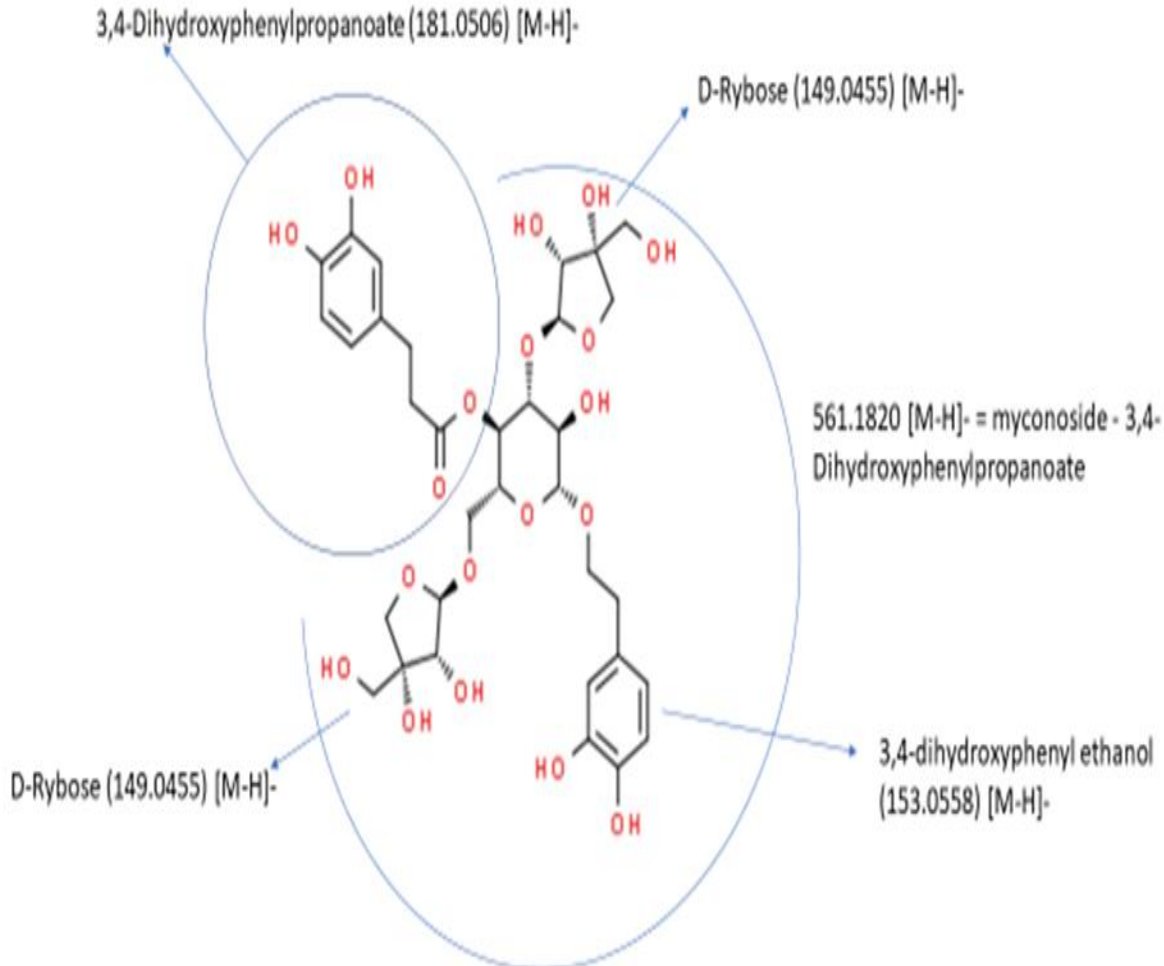

Figure S1. Molecular structure of Myconoside and detected ion fragments derived from MS/MS spectra

Table S3. Metabolic content of fraction18. On the first row is (Hispidulin 8-C-(6-O-acetyl-2”-O-syringoyl-β-glu- copyranoside) is 23 % of total metabolic content).

Peak	RT	Area	% TIC
38	22.012	6016968389	23.54
30	17.162	2857998612	11.18
31	17.561	2252716780	8.81
14	10.252	2124392381	8.31
37	19.92	1451705932	5.68
29	16.929	927731971.1	3.63
15	10.567	865334482.3	3.39
36	19.089	783676763	3.07
25	15.302	757935325.4	2.97
23	14.87	620549011.3	2.43
39	22.411	509322356.5	1.99
19	12.228	470694759.6	1.84
27	15.584	470103697.1	1.84
41	23.292	448423423.1	1.75
1	0.999	430426965.7	1.68
48	33.392	278556598.9	1.09
22	14.537	273787696.3	1.07
13	9.836	230522777.1	0.90
43	24.471	225102941.1	0.88
26	15.434	224089694.5	0.88
35	18.375	215313898.1	0.84
40	22.993	207708178.1	0.81
6	8.175	196976617.5	0.77
47	30.269	159797118.7	0.63
44	24.654	157486189.6	0.62
18	11.697	157243071.2	0.62
42	23.757	156005424.1	0.61
2	2.062	149959961.5	0.59
7	8.275	145348865.2	0.57
21	12.793	136662512.6	0.53
17	11.58	130892297.9	0.51
8	8.79	115074511.4	0.45
32	17.976	110770993	0.43
33	18.076	109939278.6	0.43

16	**10.8**	**107783871.3**	**0.42**
49	**33.558**	**103170704.8**	**0.40**
3	**4.039**	**97510129.63**	**0.38**
10	**9.437**	**93006070.65**	**0.36**
24	**15.019**	**87295615.83**	**0.34**
9	**9.105**	**85254578.72**	**0.33**
28	**16.049**	**82138815.93**	**0.32**
12	**9.67**	**75896934.35**	**0.30**
5	**7.378**	**74850812.65**	**0.29**
20	**12.478**	**67505384.39**	**0.26**
4	**6.73**	**66980294.99**	**0.26**
46	**29.172**	**63870656.48**	**0.25**
11	**9.57**	**61671016.44**	**0.24**
34	**18.275**	**61161396.86**	**0.24**
45	**25.019**	**60859657.28**	**0.24**

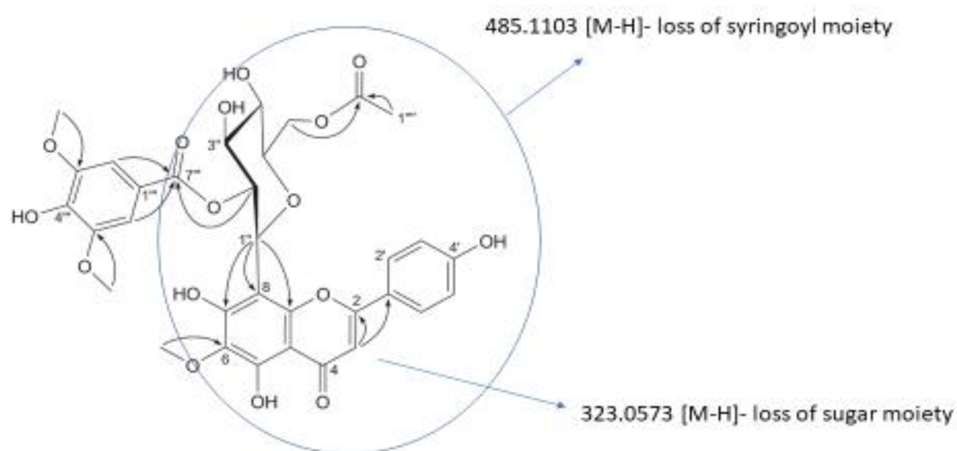

Figure S2. Molecular structure of Hispidulin 8-C-(6-O-acetyl-2”-O-syringoyl-β-glu- copyranoside) and detected ion fragments derived from MS/MS spectra

NMR identification of Myconoside and Hispidulin 8-C-(6-O-acetyl-2”-O-syringoyl-β-glu- copyranoside)

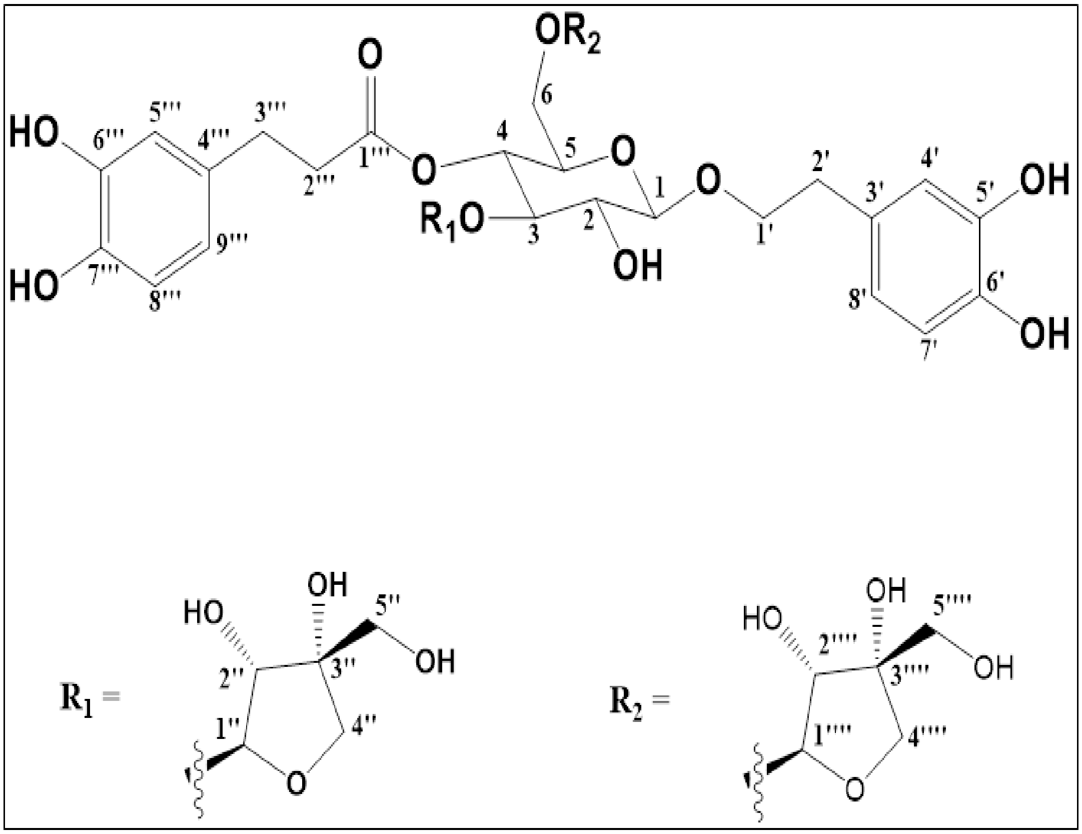

Figure S3. Structure of myconoside. * From Salvador Canigueral, Marıa Jose Salvıa, Roser Vila, Jose Iglesias, Albert Virgili and Teodor Parella, "New Polyphenol Glycosides from Ramonda myconi", J. Nat. Prod. 1996, 59, 419-422.

Table S4. Table of signals of ^{1}H and ^{13}C of Myconoside in the present study and previously published (the table is on the next page)

Position	Literature in Ac-d_6*		This work in MeOH-d_4	
	^{1}H	^{13}C	^{1}H	^{13}C
1	4.38 (d,7.8)	103.60	4.41 (d,8.0)	102.32
2	3.39 (t,7.6)	75.40	3.40 (dd,8.1,9.2)	73.4
3	3.70 (dd,9.5,7.5)	80.60	3.68 (t,9.2)	81.8
4	4.78 (dd,9.5,10.0	70.40	4.84 (dd,ov.)	69.32
5	3.62 (ddd,2.5,6.4,10.0)	74.10	3.58 (m)	72.48
6	3.55 (dd,11.5,2.5)	67.70	3.51 (dd,2.2,11.5)	66.3
	3.36 (dd,11.5,6.4)		3.22 (dd,5.5,11.5)	
1'	3.95 (ddd,6.9,7.7,9.7)	71.50	4.01 (ddd,6.8,7.8,14.7)	71.05
	3.68 (ddd,7.0,7.7,9.5)		3.78 (ddd,7.0,8.0,14.7)	
2'	2.75 m	36.20	2.81 (m)	34.82
3'		131.10		130.78
4'	6.75 (d,2.1)	116.30	6.78 (d,2.1)	116
5'		145.60		142.9
6'		144.20		144.5
7'	6.70 (d, 8.0)	116.10	6.79 (d,8.0)	116
8'	6.58 (dd,2.1,8.0)	121.00	6.66 (dd,2.1,8.0)	120.68
1''	5.35 (d,1.9)	111.00	5.24 (d,2.9)	110.41
2''	3.88 (br.)	77.60	3.95 (d,2.9)	76.94
3''		80.10		81.88
4''	3.85 (d,9.5)	74.80	3.82 (d,9.9)	73.44
	3.69 (d,9.5)		3.76 (d,9.9)	
5''	3.53 (br.)	65.70	3.58 (m)	63.59
1'''		172.60		173.5
2'''	2.65 (m)	36.80	2.71 (m)	35.74
3'''	2.80 (m)	30.70	2.82 (m)	29.43
4'''		133.30		132.36
5'''	6.73 (d,2.1)	116.20	6.75 (d,2.1)	115.75
6'''		145.70		142.9
7'''		144.20		144.5
8'''	6.71 (d,8.0)	115.90	6.80 (d,8.0)	116
9'''	6.55 (dd,2.1,8.0)	120.30	6.63 (dd,2.1,8.0)	119.98
1''''	4.90 (d,2.0)	110.50	4.84 (d,2.7)	109.14
2''''	3.90 (br.)	77.70	3.91 (d,2.7)	76.67
3''''		80.10		81.75
4''''	3.91 (d,9.5)	74.60	3.95 (d,10.0)	73.64
	3.72 (d,9.5)		3.82 (d,10.0)	
5''''	3.58 (br.)	65.50	3.62 (m)	63.98

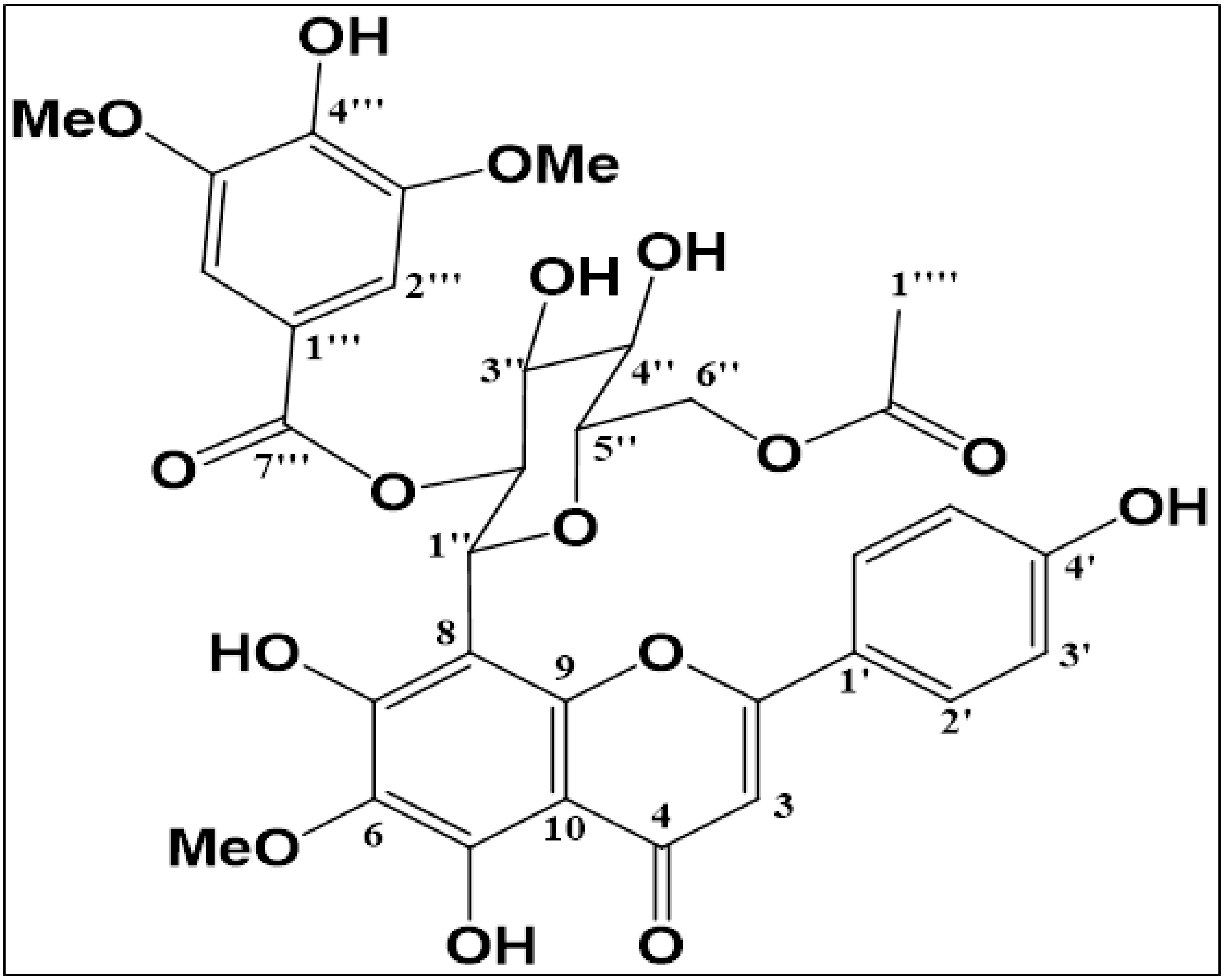

Figure S4. Structure of Hispidulin 8-C-(6-O-acetyl-2”-O-syringoyl-β-glucopyranoside)

*** From Samad N. Ebrahimia, Frank Gafner, Giorgio Dell'Acqua, Kuno Schweikert, and Matthias Hamburger "Flavone 8-C-Glycosides from Haberlea rhodopensis Friv. (Gesneriaceae)", Helvetica Chimica Acta – Vol. 94 (2011) 38.**

Table S5. Table of ^{1}H signals of Hispidulin 8-C-(6-O-acetyl-2”-O-syringoyl-β-glucopyranoside) in the present study and previously published

Position	literature in DMSO-d_6*	This work in $CDCl_3$
3	6.73	6.81 s
2’,6’	8.34 (d, 8,6)	8.36 (d,8.8)
3’,5’	6.91 (d, 8,6)	7.03 (d, 8.8)
1’’	5.14 (d, 10,1)	5.25 (d, 10.1)
2’’	5.8 (dd,10,1;10,3)	6.00 (t, 9.9)
3’’	3.92 (dd,10,3;7,6)	4.14* m
4’’	3.98 9dd,unses.)	4.25* m
5’’	4,00 (m)	4.14 *m
6’’a	4.32 (dd, 11,5;3,5)	4.45* m
6’’b	4,18 (dd, 11,5;7,2)	4.25* m
2’’’,6’’’	7,00	7.15 s
Me-1’’’’	2,00	2.09 s
MeO-6	3.48	2.50 s
MeO-3’’’,5’’’	3.77	3.87 s