Supporting Information

New Resistance-Correlated Saponins from the Insect Resistant Crucifer *Barbarea vulgaris*

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Supporting Information Table 2. NMR spectroscopic data of **2**

Pos.	$^{13}C^{a}$	$^{1}H^{a,b}$	NOESY[a,c,d]	HMBC[a,c,e]
1	39.3	ax: 0.96 (*td*, $J_{1ax,1eq} = J_{1ax,2ax} = 13.3$, $J_{1ax,2eq} = 3.4$)	1eq, 2eq, 3, 9	9, 10
		eq: 1.61 (*br d*, $J_{1eq,1ax} = 13.3$)	1ax, 2ax, 2eq, 11α, 25	3, 5, 10, 25
2	26.1	ax: 1.73 (*br qd*, $J_{2ax,2eq} \approx J_{2ax,1ax} \approx J_{2ax,3ax} = 13.4$, $J_{2ax,1eq} \approx 3.4$)	1eq, 2eq, 24, 25	3
		eq: 1.92 (*m*)	1ax, 1eq, 2ax, 3, 1'	3
3	83.2	3.62 (*dd*, $J_{3ax,2ax} =12.0$, $J_{3ax,2eq} = 4.8$)	1ax, 2eq, 5, 1'	4, 23, 24, 1'
4	43.6			5, 23A, 23B, 24
5	47.9	1.23 (*dd*, $J_{5ax,6ax} = 12.0$, $J_{5ax,6eq} \approx 1.2$)	3, 7ax, 9, 23A, 23B, 27, 1'	1, 3, 4, 6, 7, 9, 10, 16, 23, 24, 25
6	18.7	ax: 1.37 (*qd*, $J_{6ax,6eq} \approx J_{6ax,5ax} \approx J_{6ax,7ax} = 13.0$, $J_{6ax,7eq} = 3.0$)	6eq, 24, 25, 26	
		eq: 1.48 (*br dt*, $J_{6eq,6ax} = 13.0$, $J_{6eq,5ax} \approx J_{6eq,7ax} \approx J_{6eq,7eq} \approx 3.0$)	5ax, 6ax, 7eq, 23A, 23B, 24	5, 7, 10
7	33.3	ax: 1.60 (*br t*, $J_{7ax,7eq} \approx J_{7ax,6ax} = 13.0$)	5, 7eq, 27	5, 6, 8, 14
		eq: 1.27 *dt*, $J_{7eq,7ax} = 13.0$, $J_{7eq,6ax} \approx J_{7eq,6eq} = 3.0$	6eq, 7ax	5, 6, 8, 14
8	48.5			26, 27
9	48.9	ax: 1.63 (*m*)	1ax, 5, 11α, 27	1/14, 5/8, 10, 11, 26
10	37.4			5, 9, 25
11	24.2	α: 1.88 (*m*)	1ax, 1eq, 9, 12, 27	9, 12, 13
		β: 1.91 (*m*)	12, 25, 26	9, 12, 13
12	122.6	5.22 (*t*, $J_{12,11\alpha} = J_{12,11\beta} = 3.5$)	11α, 11β, 18, 19eq,	9, 11, 13, 18, 27
13	146.0			11, 12, 18, 19, 27

14	40.2			12, 15, 16, 26, 27
15	28.8	ax: 1.83 (*dt*, $J_{15ax,15eq} \approx J_{15ax,16ax} = 13.6$, $J_{15ax,16eq} = 3.0$)	7eq, 15eq, 16eq, 26	14, 16, 27
		eq: 1.02 (*dt*, $J_{15eq,15ax} = 13.6$, $J_{15eq,16ax} \approx J_{15eq,16eq} = 3.0$)	7eq, 15ax, 16eq, 27	13, 14, 16, 27
16	24.0	ax: 1.93 (*m*)	15eq, 16eq, 19ax, 21ax, 27	15, 17, 28
		eq: 1.59 (*br d*, $J_{16eq,16ax} = 13.6$)	7eq, 15ax, 15eq, 16ax	15, 17
17	48.3			15, 16, 18, 19, 21, 22
18	42.9	2.88 (*dd*, $J_{18,19ax} = 13.6$, $J_{18,19eq} = 4.2$)	12, 19eq, 22ax, 30	12, 13, 16, 17, 19
19	47.5	ax: 1.67 (*t*, $J_{19ax,19eq} = J_{19ax,18} = 13.8$)	16ax, 19eq, 21ax	13, 18, 20, 21, 29, 30
		eq: 1.10 (*dm*, $J_{19eq,19ax} = 13.8$)	12, 18, 19ax, 29, 30	13, 18, 20, 21, 29, 30
20	31.3			19, 29, 30
21	35.0	ax: 1.37 (*dt*, $J_{21ax,21eq} \approx J_{21ax,22ax} = 13.9$, $J_{21ax,22eq} = 3.2$)	16ax, 19ax, 21eq, 22eq, 29	19, 22, 29, 30
		eq: 1.16 (*br d*, $J_{21eq,21ax} = 13.9$)	21ax, 29, 30	19, 22, 29, 30
22	33.9	ax: 1.73 (*m*)	18, 22eq, 30	18, 19, 20, 28, 30
		eq: 1.51 (*dt*, $J_{22eq,22ax} = 13.6$, $J_{22eq,21ax} \approx J_{22eq,21eq} = 3.2$)	16ax, 21eq, 22ax	17, 18, 20, 30
23	64.6	A: 3.28 (*d*, $J_{23A,23B} = 11.4$)	3, 5, 6ax, 6eq, 23B, 24, 1'	3, 4, 5, 24
		B: 3.62 (*d*, $J_{23B,23A} = 11.4$)	5, 6eq, 23A, 24	3, 5, 5, 24
24	13.2	0.70 (*s*)	2ax, 6ax, 6eq, 23A, 23B, 25	3, 4, 5, 23
25	16.0	0.98 (*s*)	1eq, 2ax, 11β, 24, 26	1, 5, 9, 10
26	17.8	0.85 (*s*)	6ax, 11β,15ax, 25	7, 8, 14
27	26.2	1.16 (*s*)	5, 7ax, 9, 15eq, 16ax, 19ax	14, 15
28	184.1			16, 18, 22

29	33.6	0.89 (*s*)	19eq, 21ax, 21eq	19, 20, 21, 30
30	23.8	0.94 (*s*)	12, 18, 19eq, 21eq	19, 20, 21, 29
1'	105.4	4.42 (*d*, $J_{1',2'}$ = 7.9)	2eq, 3, 5, 23A, 23B, 24, 3', 5'	3, 5'
2'	75.1	3.23 (*dd*, $J_{2',3'}$ = 9.2, $J_{2',1'}$ = 7.9)	4'	1', 3'
3'	76.4	3.49 (*t*, $J_{3',2'} = J_{3',4'}$ = 9.2)	1', 5', 1"	2', 4'
4'	80.3	3.56 (*br dd*, $J_{4',3'}$ = 9.2, $J_{4',5'}$ = 9.5)	2', 6', 1", 2"	3', 5',6', 1"
5'	76.0	3.39 (*dt*, $J_{5',4'}$ = 9.5, $J_{5',6'A} = J_{5',6'B}$ = 3.1)	1', 3', 6'	
6'	61.8	3.86 (*m*)	4', 5', 1", 2"	4', 5'
1"	104.4	4.41 (*d*, $J_{1",2"}$ = 7.9 Hz)	3', 4', 6', 3", 5"	4', 3"
2"	74.7	3.21 (*dd*, $J_{2",3"}$ = 9.2, $J_{2",1"}$ = 7.9)	4', 6'	1", 3", 4"
3"	77.6	3.36 (*t*, $J_{3",2"} \approx J_{3",4"}$ = 9.0)	1"	2", 4"
4"	71.1	3.29 (*m*)		3", 5", 6"
5"	77.8	3.33 (*ddd*, $J_{5",4"}$ = 9.7, $J_{5",6"A}$ = 5.8, $J_{5",6"B}$ = 2.1)	1", 6"A, 6"B	4"
6"	62.2	A: 3.65 (*dd*, $J_{6"A,6"B}$ = 12.0, $J_{6"A,5"}$ = 5.8)	6"B	4", 5"
		B: 3.87 (*dd*, $J_{6"A,6"B}$ = 12.0, $J_{6"B,5"}$ = 2.1)	5", 6"A	4", 5"

[a] ^{1}H (800 MHz) and ^{13}C (200 MHz) NMR spectroscopic data measured in methanol-d_4, δ values relative to internal TMS. [b] Multiplicity of signals is given in parentheses: *s*, singlet; *d*, doublet; *t*, triplet; *q*, quartet; *m*, multiplet; *br*, broad; coupling constants (apparent splittings) are reported as numerical values in Hz. [c] Signal correlating with ^{1}H resonance. [d] Mixing time 600 ms. [e] Optimized for $^nJ_{C,H}$ = 7.7 Hz. [f] Identified from HSQC spectrum.