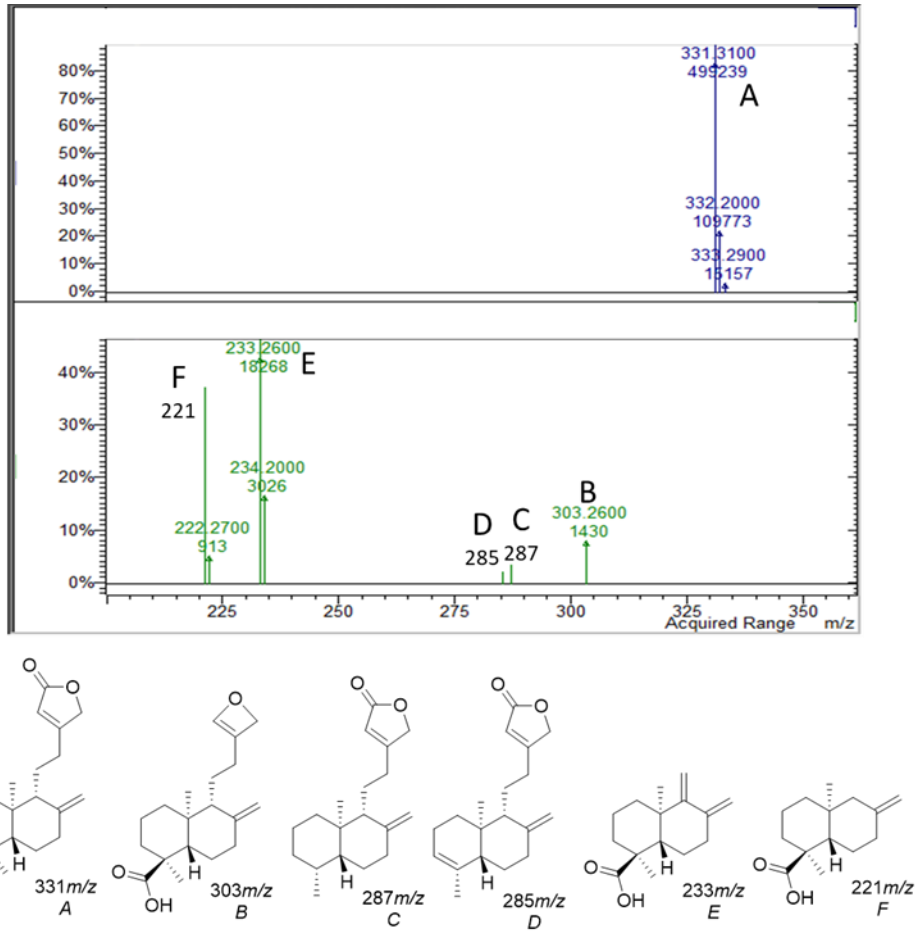
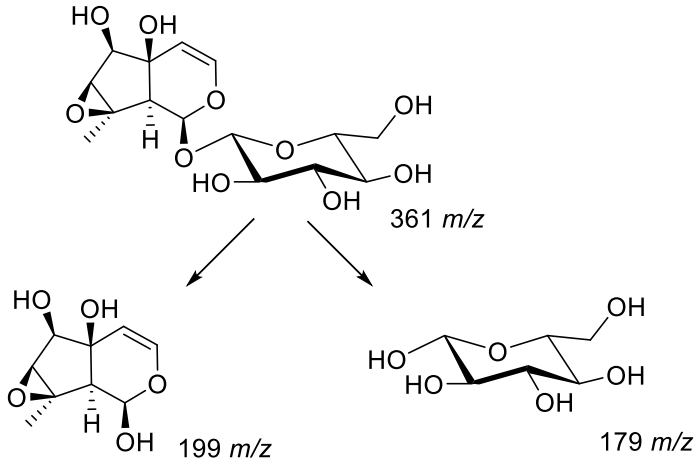
NMR, LC-MS characterization of *Rydingia michauxii* extracts, identification of natural products acting as modulators of LDLR and PCSK9.

Supplementary material:



Scheme S1. Mass spectra of compound 1 in negative ion mode (blue spectrum) and MS2 spectra (green spectrum. Proposed structures of main observed ions, indicated by letters are reported.



Scheme S2. tentatively fragmentation pathway in negative ion mode of compound 3

Table S1: NMR assignment for ent-labda-8(17),13-dien-18-oic acid-15,16-olide in deuterated chloroform

Position	δH	δC
1	1.17-1.78 m	38.1
2	1.66 m	18.5
3	1.81-1.63	35.5
4	-	47.1
5	1.97m	49.6
6	1.44 m	26.5
7	2.40-2.07m	37.6
8	-	146.2
9	1.74m	56.0
10	-	38.0
11	1.80-1.60m	21.8
12	2.57-2.27 m	27.3
13	-	171.0
14	5.88 s	114.0
15	-	174.6
16	4.76 4.72 d, *J*=18	73.9
17	4.48 *J*=1.0 β 4.92 *J*=1.0 α	105.8
18	-	185.0
19	1.17 s	16.4
20	0.75s	14.8

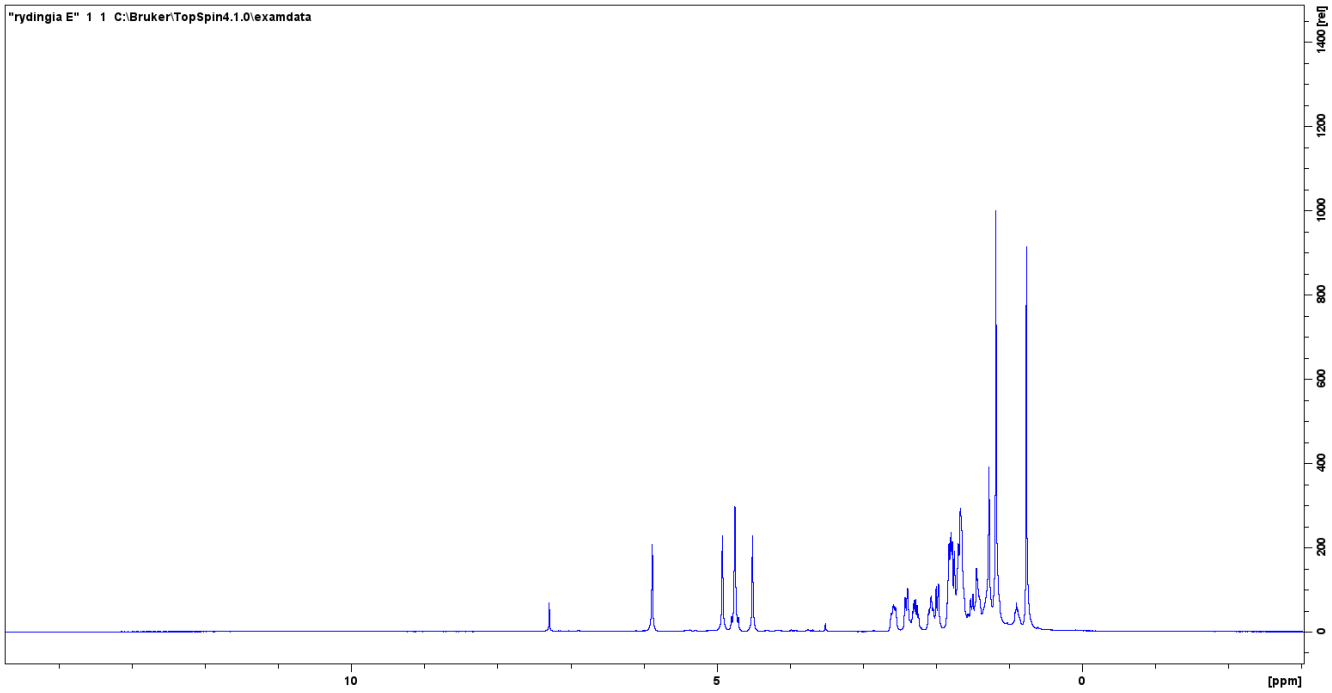


Figure S1: ^{1}H NMR of ent-labda-8(17),13-dien-18-oic acid-15,16-olide

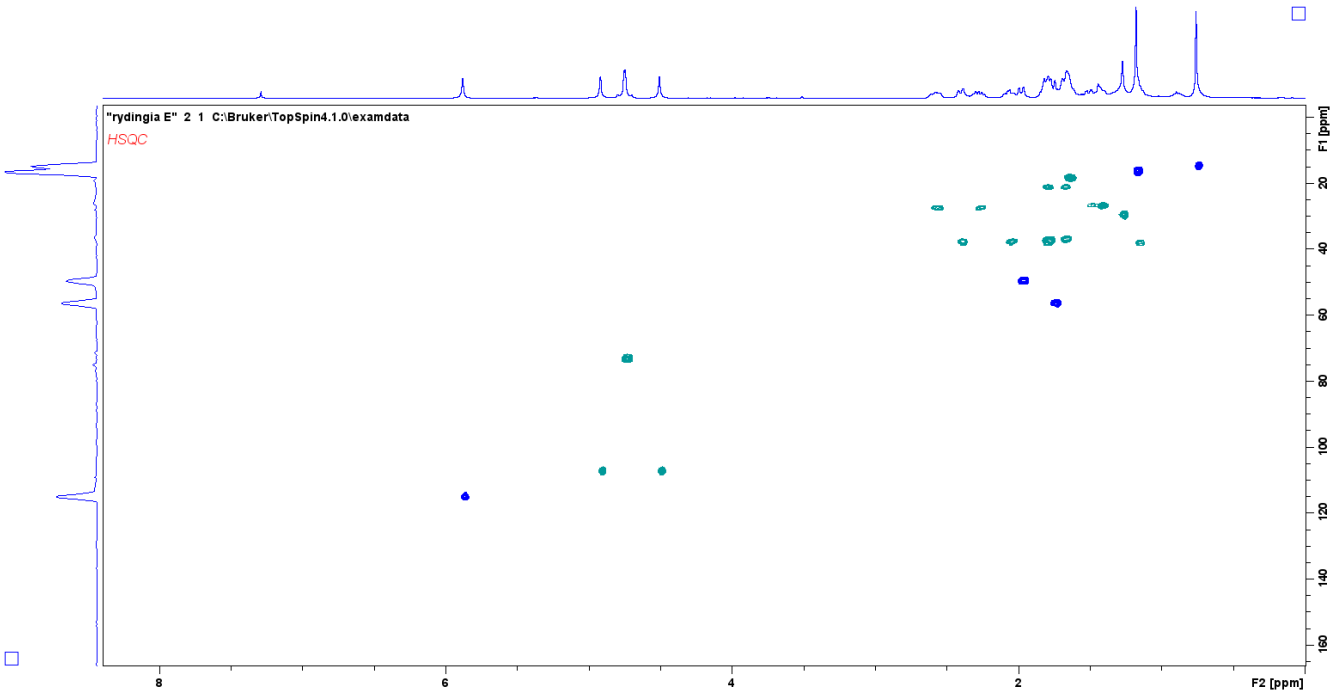


Figure S2: HSQC of ent-labda-8(17),13-dien-18-oic acid-15,16-olide

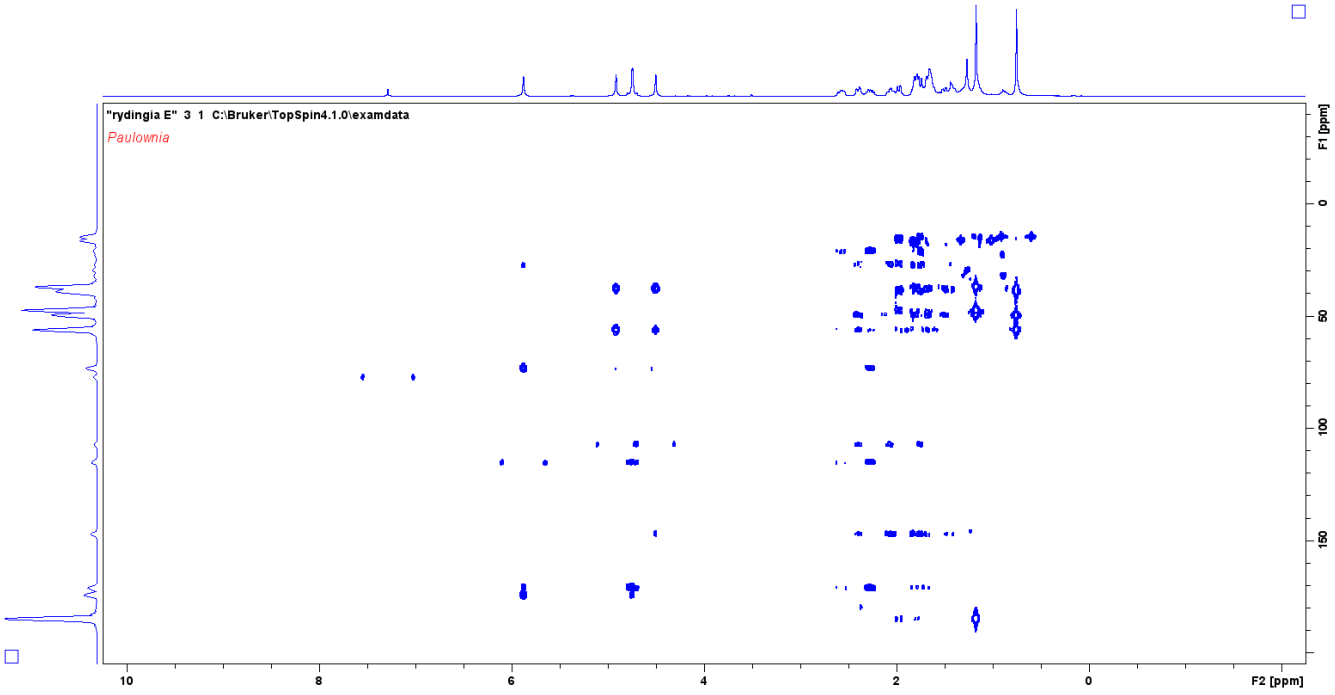


Figure S3: HMBC of ent-labda-8(17),13-dien-18-oic acid-15,16-olide

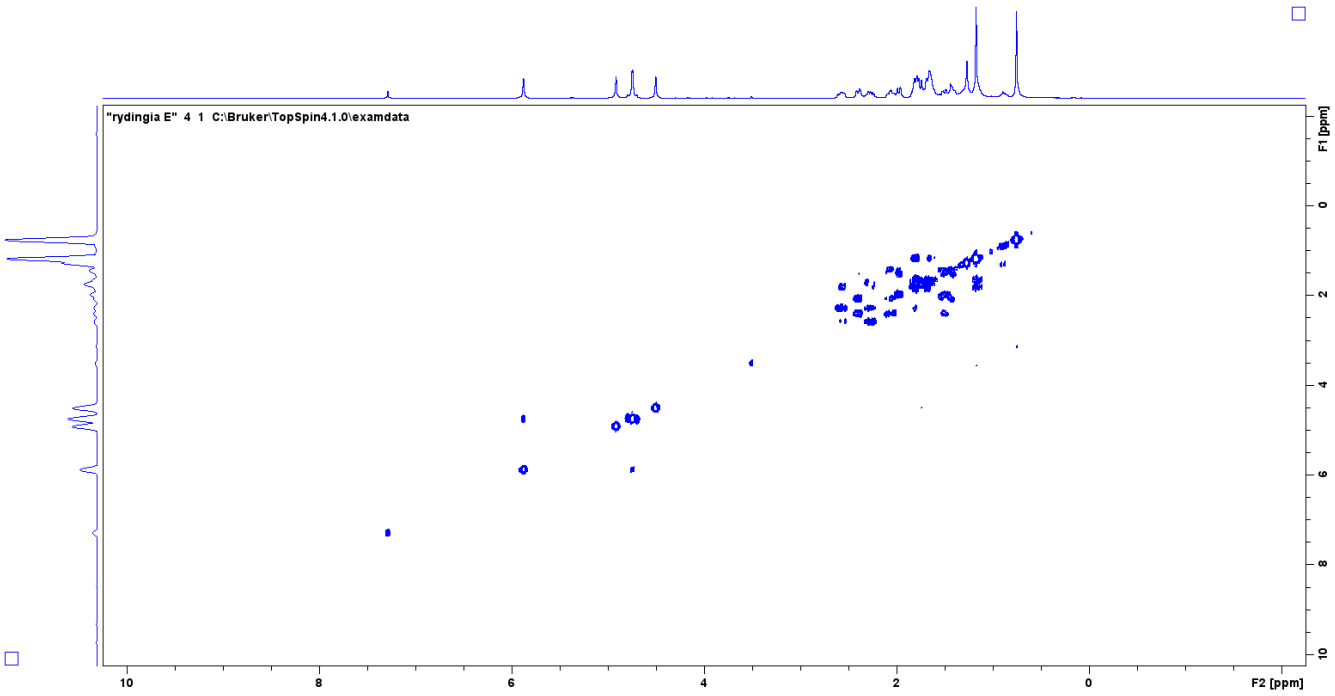


Figure S4: COSY of ent-labda-8(17),13-dien-18-oic acid-15,16-olide

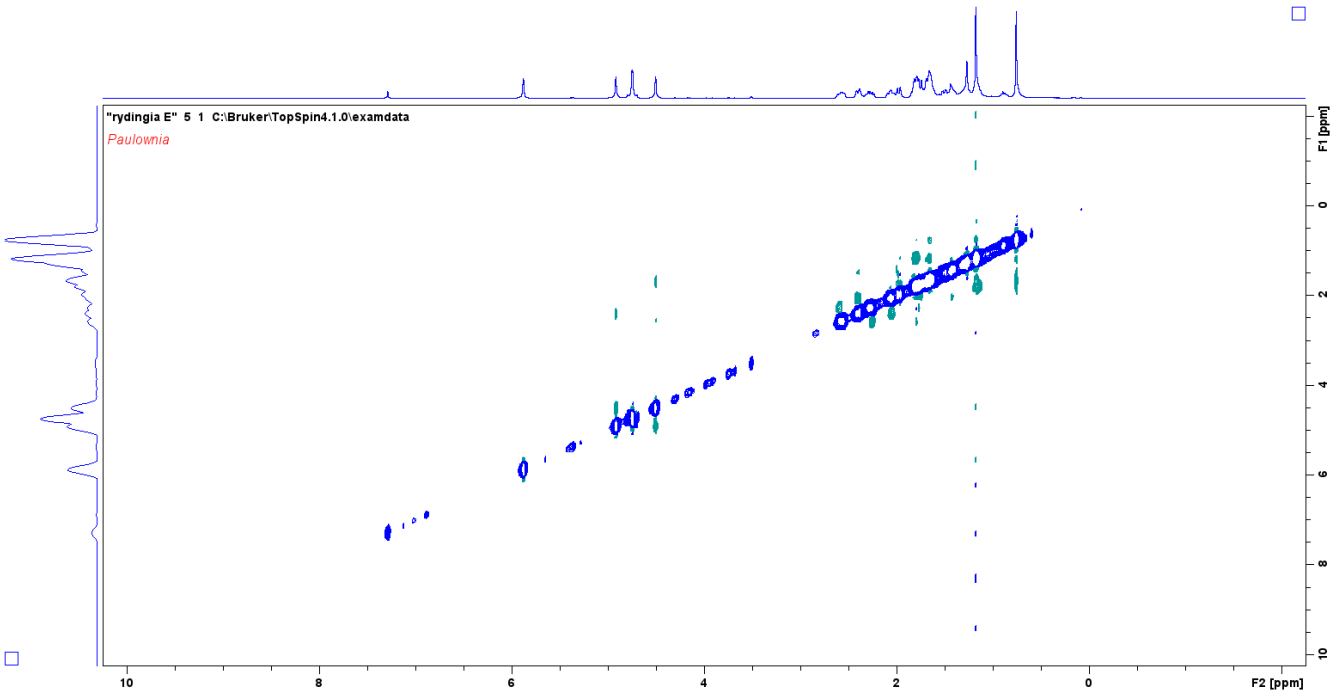


Figure S5: NOESY of ent-labda-8(17),13-dien-18-oic acid-15,16-olide

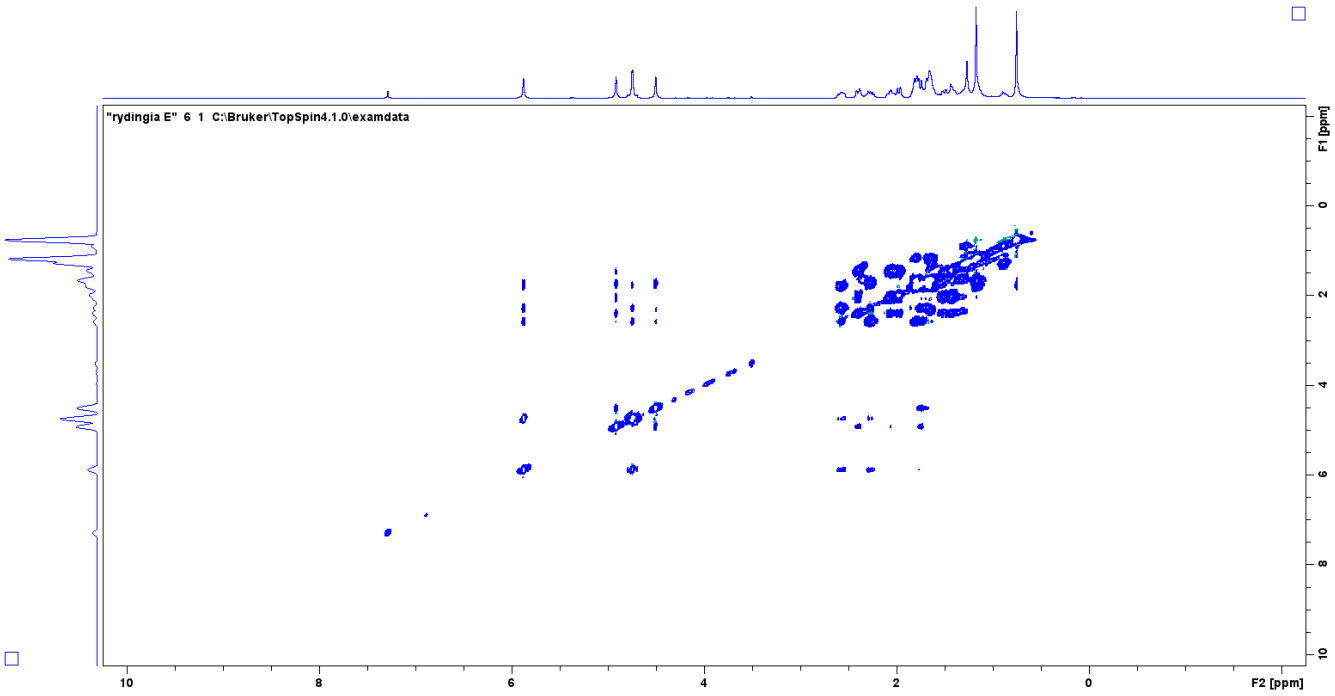


Figure S6: TOCSY of ent-labda-8(17),13-dien-18-oic acid-15,16-olide

Table S2: NMR assignment for ent-labda-8(17),13-dien-18-oic acid-15,16- glucopyranoside in deuterated methanol

Position	δH	δC
1	1.89-1.21 m	37.7
2	1.66 m	18.1
3	1.85 1.63	36.2
4	-	47.4
5	2.10 m	49.3
6	1.42m	26.4
7	2.37-2.12m	37.2
8	-	146.0
9	1.83m	56.5
10	-	38.0
11	1.85-1.74m	21.1
12	2.63-2.33 m	27.4
13	-	171.1
14	5.91 s	114.0
15	-	174.1
16	4.88 under methanol	73.5
17	4.92 *J*=1.0 β 4.58 *J*=1.0 α	106.4
18	-	177.4
19	1.20 s	15.7

20	0.79s	14.4
1′	5.45 d, *J*= 8.0	94.8
2′	3.36	72.8
3′	3.46	77.7
4′	3.41	69.9
5′	3.40	77.0
6′	3.87-3.73	61.0

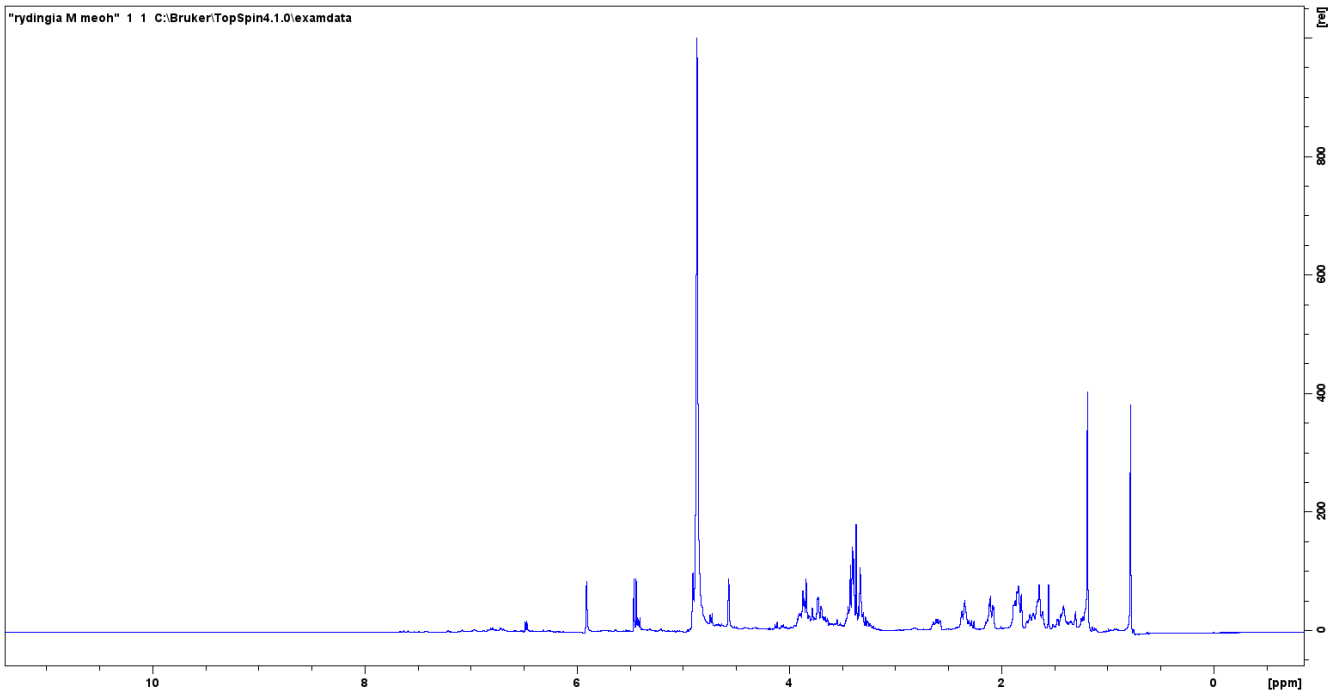


Figure S7: ^{1}H NMR of ent-labda-8(17),13-dien-18-oic acid-15,16- glucopyranoside

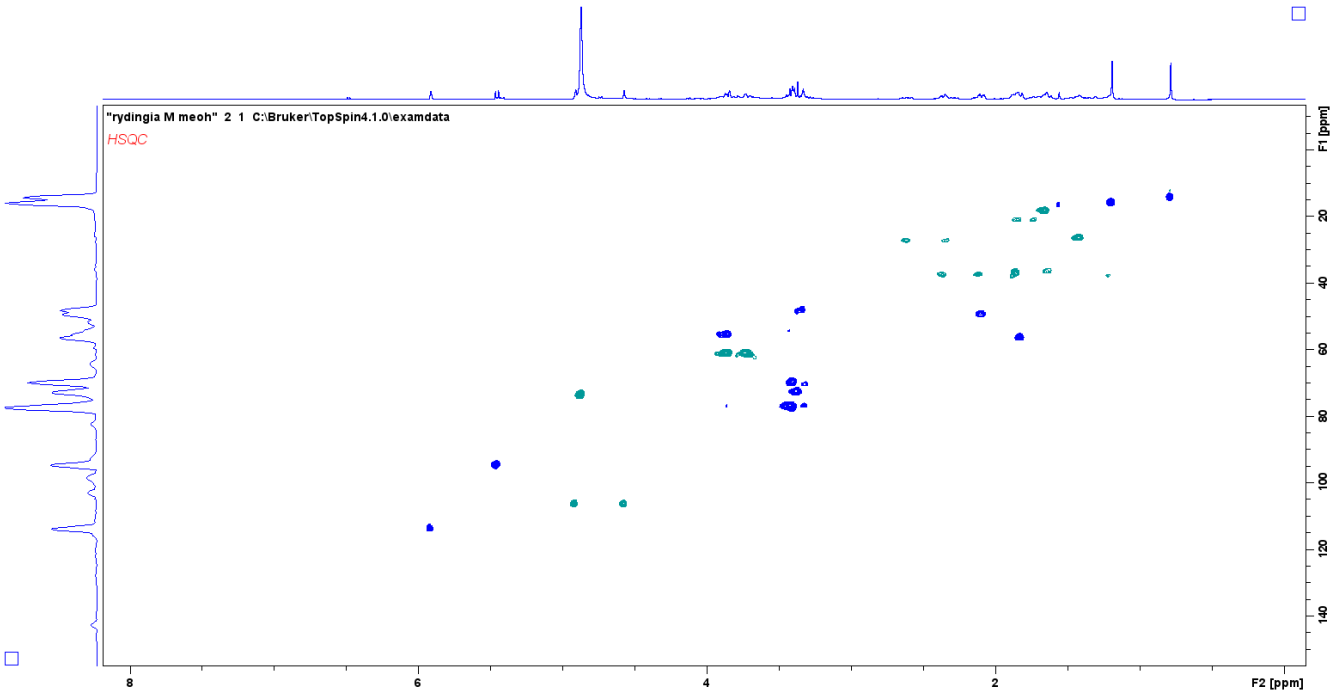


Figure S8: HSQC of ent-labda-8(17),13-dien-18-oic acid-15,16-glucopyranoside

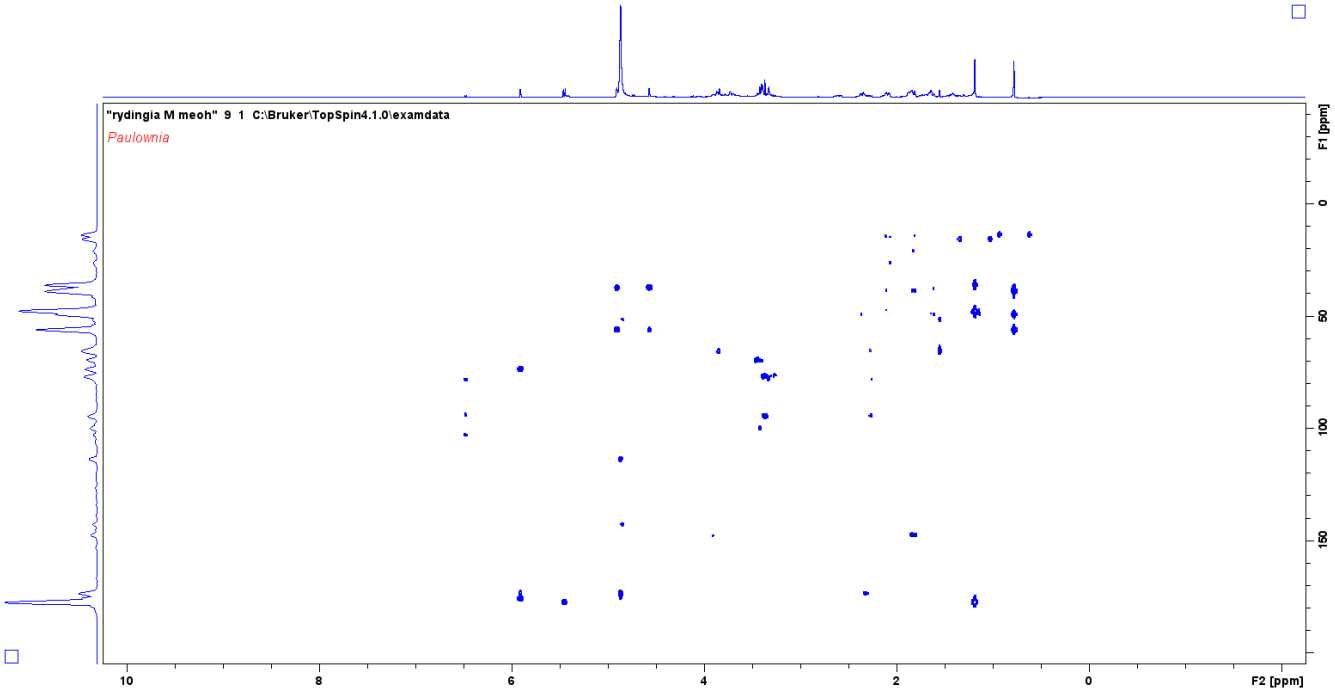


Figure S9: HMBC of ent-labda-8(17),13-dien-18-oic acid-15,16-glucopyranoside

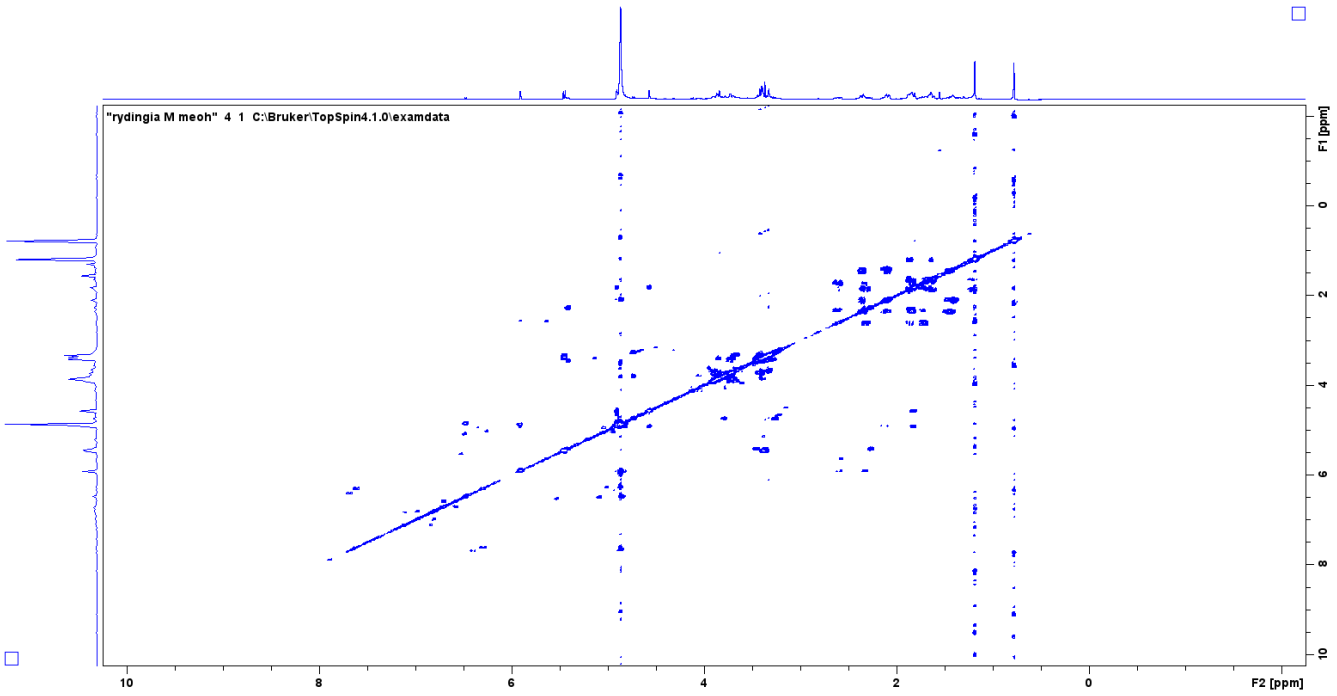


Figure S10: COSY of ent-labda-8(17),13-dien-18-oic acid-15,16-glucopyranoside

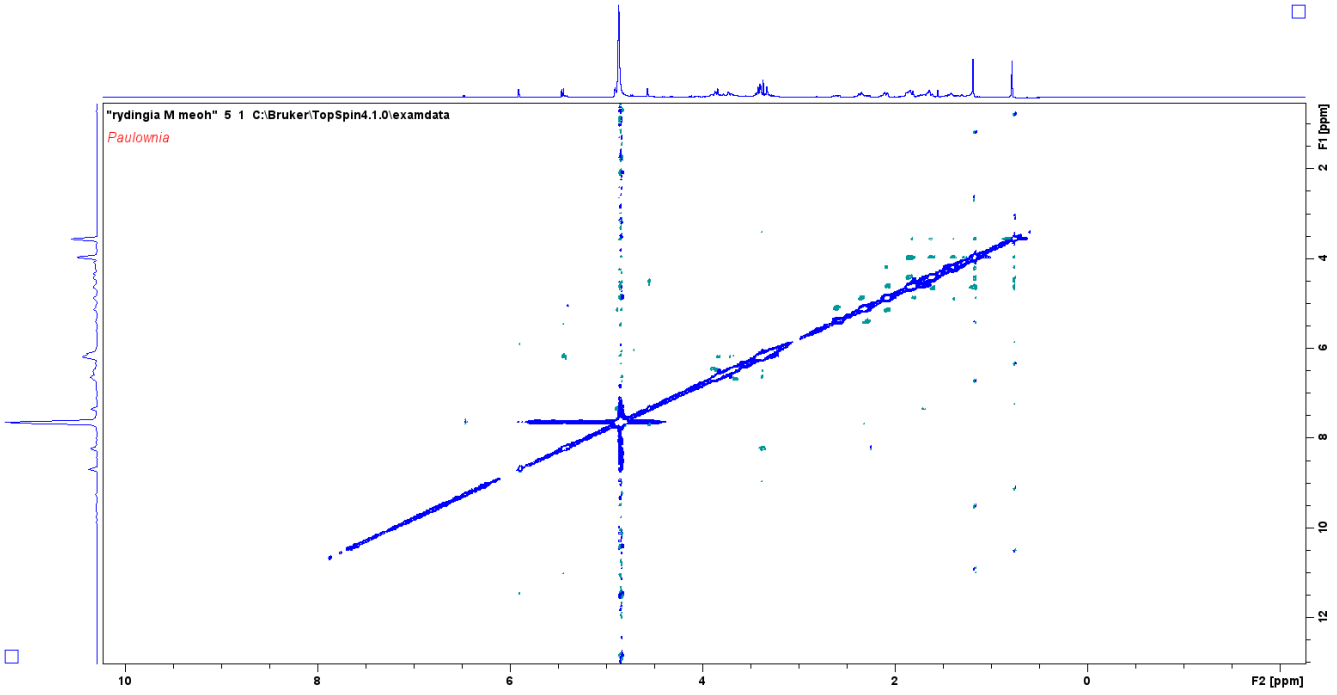


Figure S11: NOESY of ent-labda-8(17),13-dien-18-oic acid-15,16-glucopyranoside

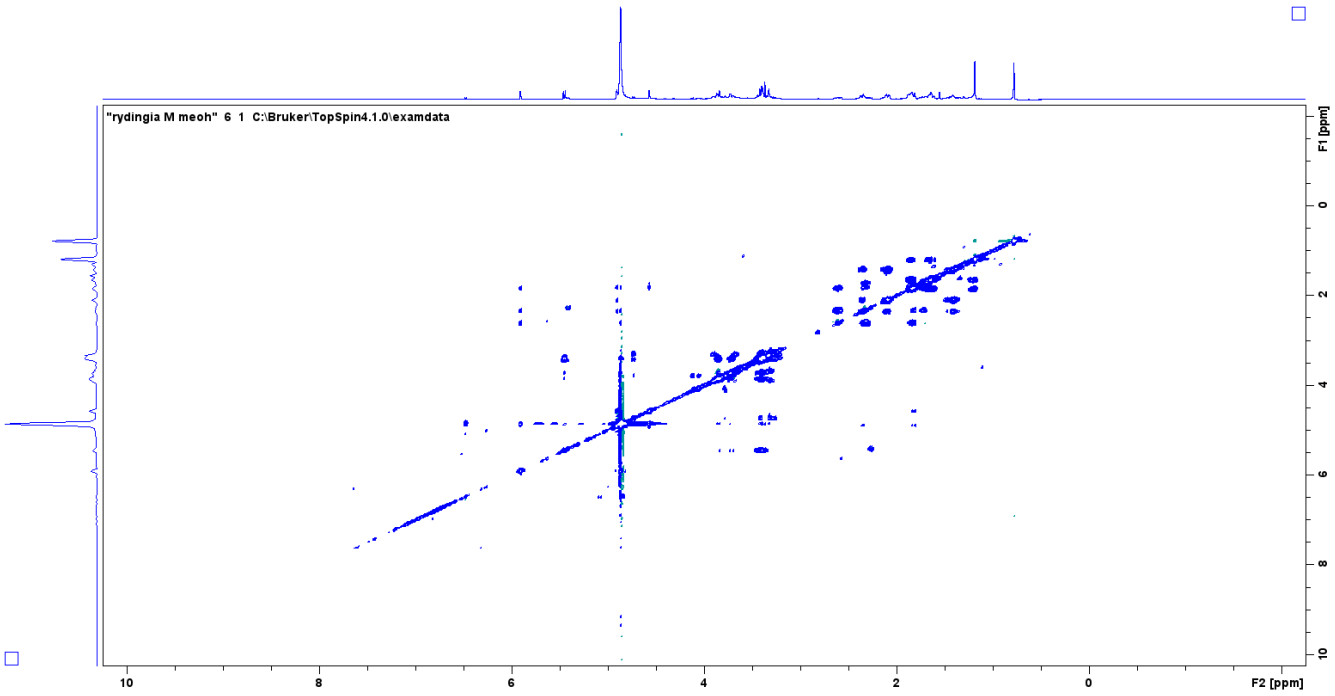


Figure S12: TOCSY of ent-labda-8(17),13-dien-18-oic acid-15,16-glucopyranoside

Table S3: NMR assignment for antirrhinoside in deuterated methanol

Position	δH	δC
1	5.41 d, *J*=8.5	94.6
3	6.48, d, *J*=6.1	142.3
4	4.84, d, under methanol signal	102.9
5	3.86 m	78.4
6	3.85 m	77.1
7	3.34 m	64.0
8	-	65.7
9	2.27 d, *J*=8.5	51.5
10	1.56 s	16.6
1′	5.43 d, *J*=8.2	94.0
2′	3.37	72.8
3′	3.39	78.9
4′	3.30	71.0
5′	3.38	77.1
6′	3.90-3.73	61.4

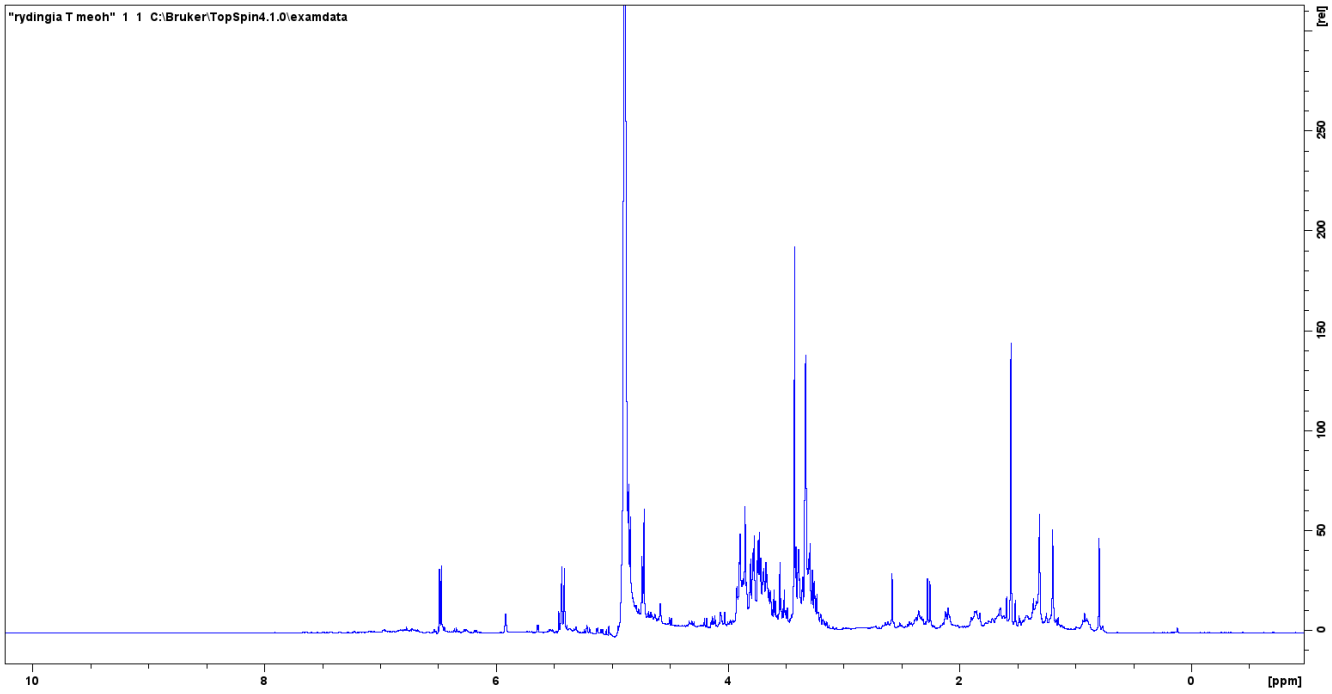


Figure S13: ^{1}H NMR of antirrhinoside

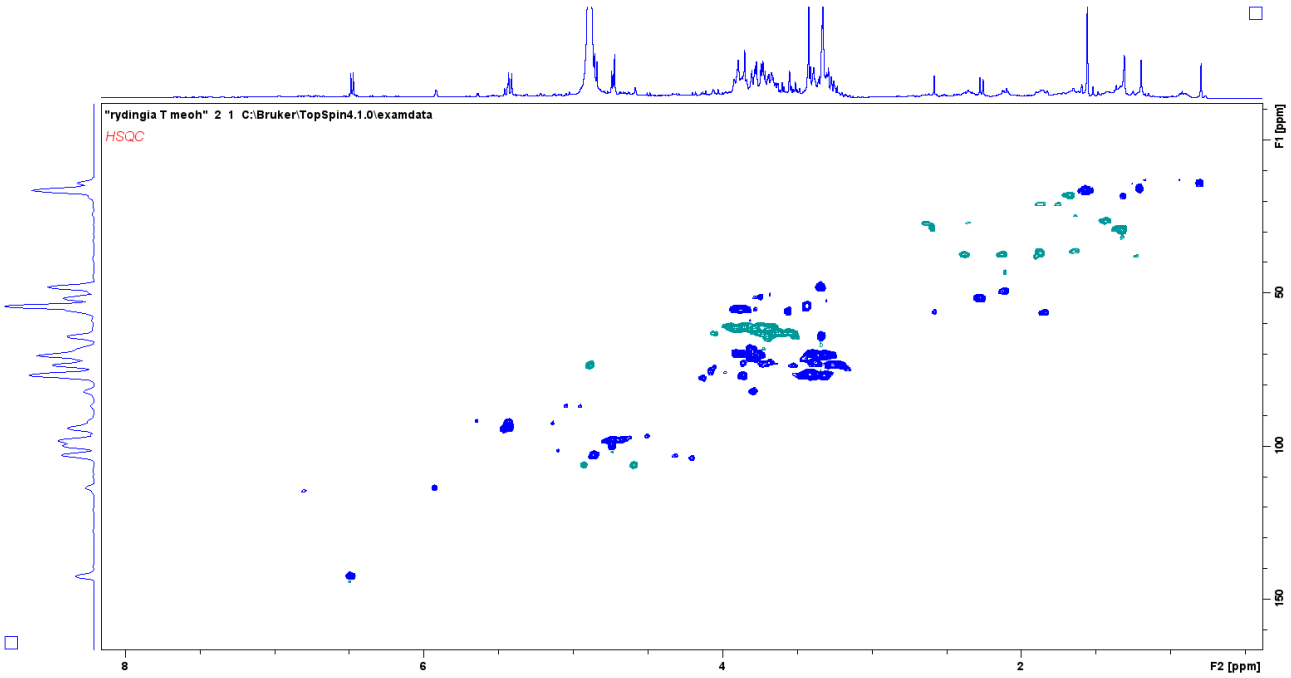


Figure S14: HSQC of antirrhinoside

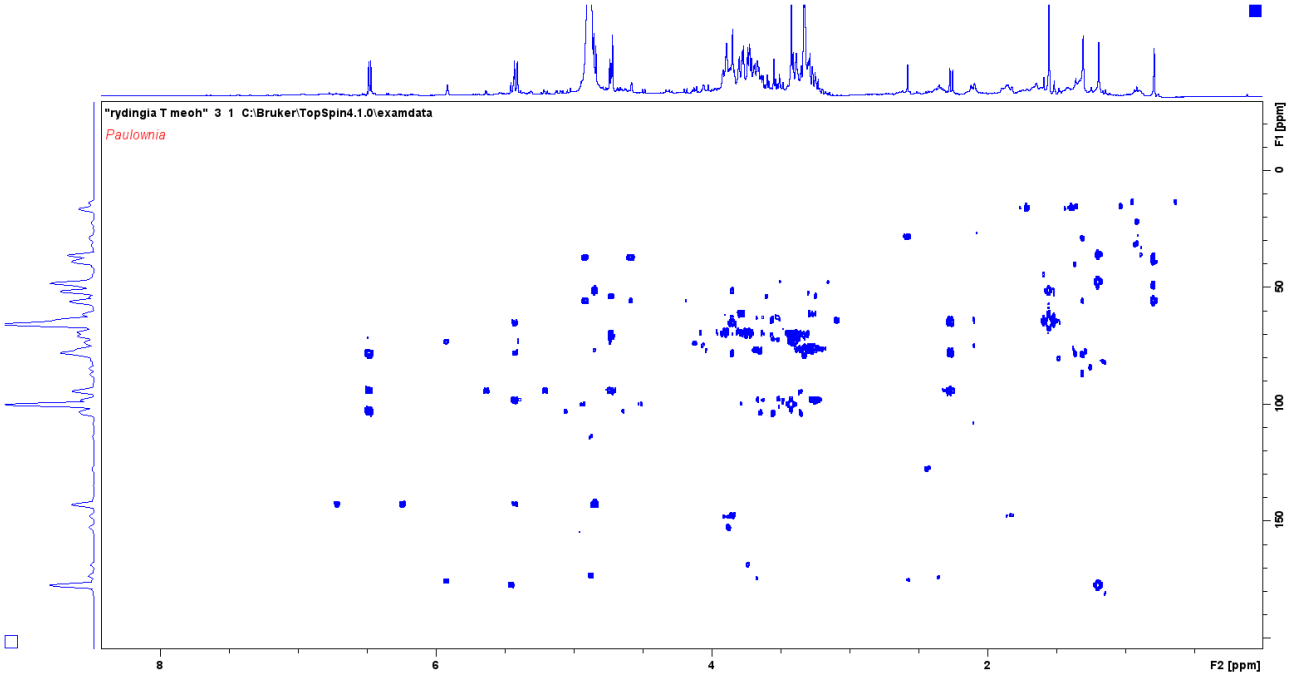


Figure S15: HMBC of antirrhinoside

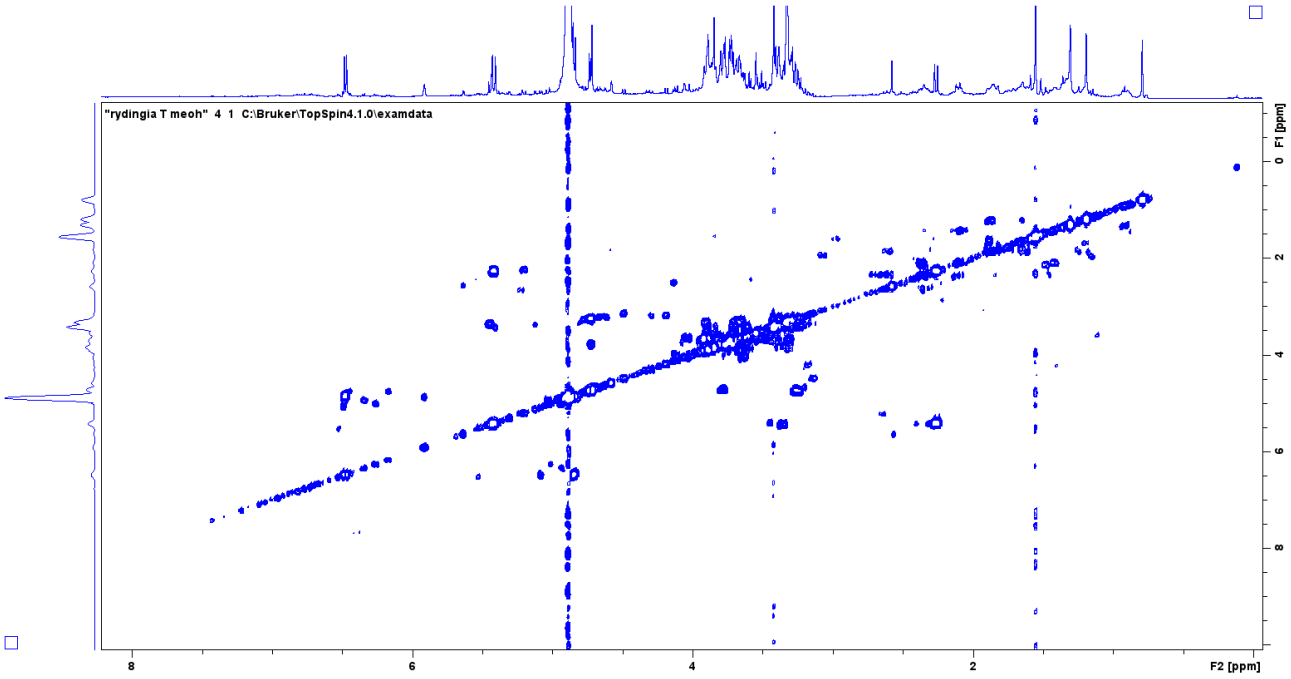


Figure S16: COSY of antirrhinoside

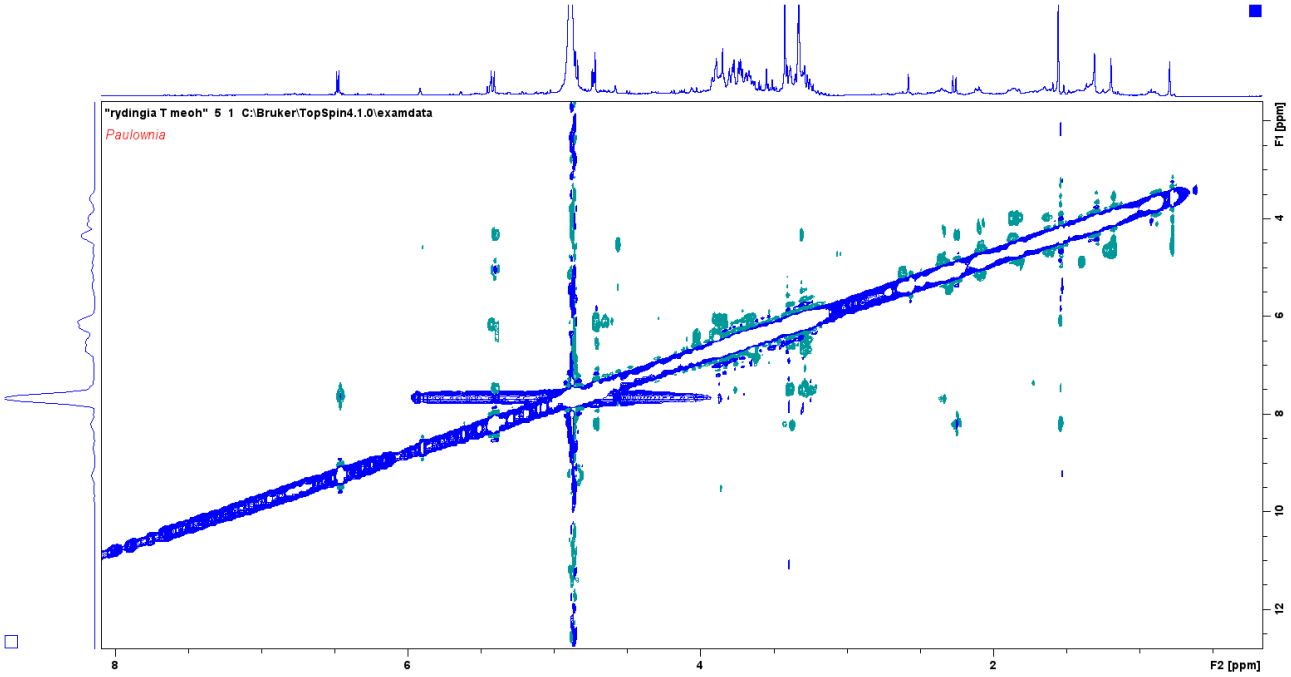


Figure S17: NOESY of antirrhinoside

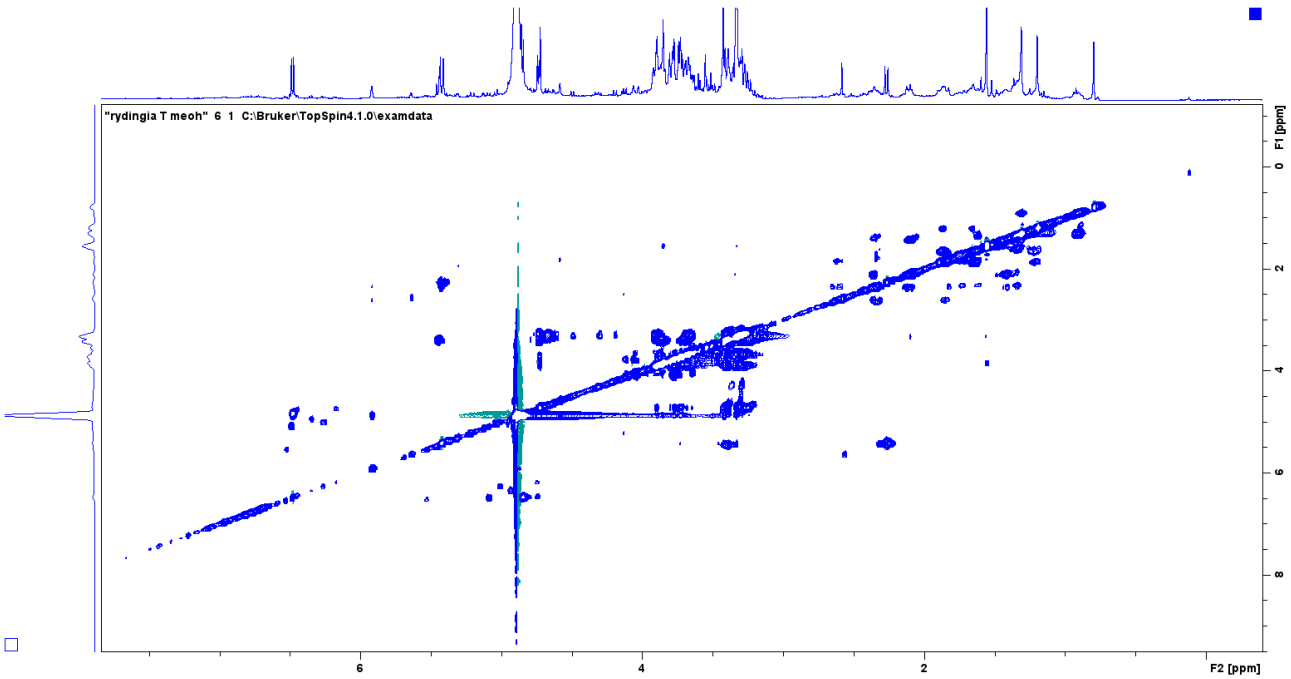


Figure S18: TOCSY of antirrhinoside