



SUPPLEMENTARY MATERIAL TO

Phytochemical investigation of *Pimpinella serbica*

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ANALYTICAL AND SPECTRAL DATA

Dillapiole (1-allyl-2,3-dimethoxy-4,5-(methylenedioxy)benzene) (**1**): ¹H-NMR and ¹³C-NMR data are given in Table S-I. (+)ESI-HRMS *m/z*: calculated for [C₁₂H₁₄O₄ + H⁺] 223.0965, observed 223.0963. EI MS 222 [M]⁺ (100) 207 (15) 177 (30) 149 (17) 121 (12) 106 (13) 91 (9) 77 (15).

Nothoapiole (1-allyl-2,3,6-trimethoxy-4,5-(methylenedioxy)benzene) (**2**): ¹H-NMR and ¹³C-NMR data are given in Table S-I. ((+)ESI-HRMS *m/z*: calculated for [C₁₃H₁₆O₅ + H⁺] 253.1071, observed 253.1082. EI MS 252 [M]⁺ (100) 237 (19) 225 (9) 221 (6) 207 (22) 191 (6) 179 (14) 164 (5) 151 (10) 121 (5) 77 (9).

Falcarindiol ((3*R*,8*S*,*Z*)-heptadeca-1,9-dien-4,6-diyne-3,8-diol) (**3**): [α]_D²⁰; *D* = +228° (*c* 0.2, CH₂Cl₂). ¹H-NMR and ¹³C-NMR data are given in Table S-II. (+)ESI-HRMS *m/z*: calculated for [C₁₇H₂₄O₂ + H⁺ - H₂O] and [C₁₇H₂₄O₂ + H⁺ - 2H₂O] 243.1743 and 225.1638, observed 243.1742 and 225.1634, respectively.

Oplopantriol A 18-acetate ((11*S*,16*R*,*Z*)-11,16-dihydroxyoctadeca-9,17-dien-12,14-diyne-1-yl acetate) (**4**): ¹H NMR and ¹³C NMR data in Table S-II. (+)ESI-HRMS *m/z*: calculated for [C₂₀H₂₈O₄ + H⁺ - 2H₂O], [C₂₀H₂₈O₄ + H⁺ - H₂O], [C₂₀H₂₈O₄ + NH₄⁺ - H₂O], [C₂₀H₂₈O₄ + NH₄⁺] and [C₂₀H₂₈O₄ + Na⁺] 297.1849, 315.1955, 332.2220, 350.2326 and 355.1880, observed 297.1863, 315.1948, 332.2213, 350.2319 and 355.1875, respectively.

Dentrotрифидол ((*R*,*Z*)-octadeca-9,17-dien-12,14-diyne-1,16-diol) (**5**): ¹H-NMR and ¹³C-NMR data are given in Table S-II. (+)ESI-HRMS *m/z*: calculated for [C₁₈H₂₆O₂ + H⁺ - H₂O], [C₁₈H₂₆O₂ + NH₄⁺] and [C₁₈H₂₆O₂ + Na⁺] 257.1900, 292.2271 and 297.1825, observed 257.1900, 292.2271 and 297.1822, respectively.

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TABLE S-I. The NMR data of phenylpropanoids from *P. serbica*

#	Dillapiole (1)		Nothoapiole (2)	
	¹ H <i>m</i> (J/Hz)	¹³ C	¹ H <i>m</i> (J/Hz)	¹³ C
1	-	126.0	-	118.7
2	-	144.6	-	136.6
3	-	137.6	-	133.3
4	-	135.9	-	137.7
5	-	144.3	-	134.5
6	6.35 <i>s</i>	102.7	-	145.0
7	5.88 <i>s</i>	101.1	5.90 <i>s</i>	101.2
8	3.30 <i>dt</i> (6.6; 1.5)	33.9	3.33 <i>dt</i> (6.1; 1.5)	28.3
9	5.91 <i>ddt</i> (16.8; 10.3; 6.6)	137.4	5.94 <i>ddt</i> (15.5; 11.5; 6.1)	137.7
10	5.04 <i>dq</i> (10.3; 1.5)	115.5	4.97 <i>dq</i> (11.5; 1.5)	114.4
-	5.05 <i>dq</i> (16.8; 1.5)	-	4.98 <i>dq</i> (15.5; 1.5)	-
2-OCH ₃	3.75 <i>s</i>	61.2	3.89 <i>s</i>	61.5
3-OCH ₃	4.01 <i>s</i>	59.9	3.94 <i>s</i>	60.4
6-OCH ₃	-	-	3.77 <i>s</i>	60.0

TABLE S-II. The NMR data of polyacetylenes from *P. serbica*

#	Falcarindiol (3)		Aplopantriol A 18-acetate (4)		Dendrotrifidiol (5)	
	¹ H <i>m</i> (J/Hz)	¹³ C	¹ H <i>m</i> (J/Hz)	¹³ C	¹ H <i>m</i> (J/Hz)	¹³ C
1	5.47 <i>dt</i> (17.2; 1.2)	117.3	5.48 <i>dt</i> (17.2; 1.2)	117.3	5.46 <i>dt</i> (17; 1.2)	116.9
	5.26 <i>dt</i> (10; 1.2)		5.26 <i>dt</i> (10; 1.2)		5.23 <i>dt</i> (10; 1.2)	
2	5.94 <i>ddd</i> (17.2; 10; 5.4)	135.8	5.94 <i>ddd</i> (17.2; 10; 5.2)	135.8	5.94 <i>ddd</i> (17; 10; 5.2)	136.2
3	4.94 <i>br t</i>	63.4	4.94 <i>br t</i> (4.8)	63.4	4.91 <i>br d</i> (5.2)	63.4
4	-	78.2	-	78.4	-	74.4
5	-	70.3	-	70.1	-	71.1
6	-	68.7	-	68.7	-	64
7	-	79.8	-	79.7	-	80.1
8	5.21 <i>br d</i> (8.1)	58.6	5.21 <i>br dd</i> (8.2; 3.0)	58.6	3.03 <i>br d</i> (7.0)	17.7
9	5.52 <i>m</i>	127.6	5.52 <i>m</i>	127.8	5.39 <i>m</i>	122
10	5.61 <i>m</i>	134.7	5.61 <i>m</i>	134.5	5.51 <i>m</i>	133
11	2.11 <i>dq</i> (7.6; 1.2)	27.6	2.12 <i>dq</i> (7.5; 1.2)	29.1	2.04 <i>br q</i> (7.2)	27
12	1.39 <i>m</i>	29.3	1.39 <i>m</i>	29.2	1.38 <i>m</i>	28.9
13	1.28 <i>m</i>	29.15	1.29 <i>m</i>	29	1.29 <i>m</i>	29.4
14	1.27 <i>m</i>	29.1	1.29 <i>m</i>	28.9	1.29 <i>m</i>	29.3
15	1.27 <i>m</i>	31.8	1.29 <i>m</i>	28.6	1.29 <i>m</i>	29
16	1.27 <i>m</i>	22.6	1.29 <i>m</i>	27.6	1.29 <i>m</i>	25.6
17	0.88 <i>t</i> (7.1)	14.1	1.60 <i>m</i>	25.8	1.57 <i>m</i>	32.7
18	-	-	4.06 <i>t</i> (6.7)	64.7	3.64 <i>t</i> (6.7)	63.1
19	-	-	-	171.4	-	-
20	-	-	2.05 <i>s</i>	21	-	-
3-OH	2.01 <i>bd d</i>	-	2.20 <i>br d</i> (6.4)	-	1.62 <i>br s</i>	-
8-OH	1.91 <i>bd s</i>	-	1.94 <i>bd d</i> (4.2)	-	-	-
18-OH	-	-	-	-	1.62 <i>br s</i>	-

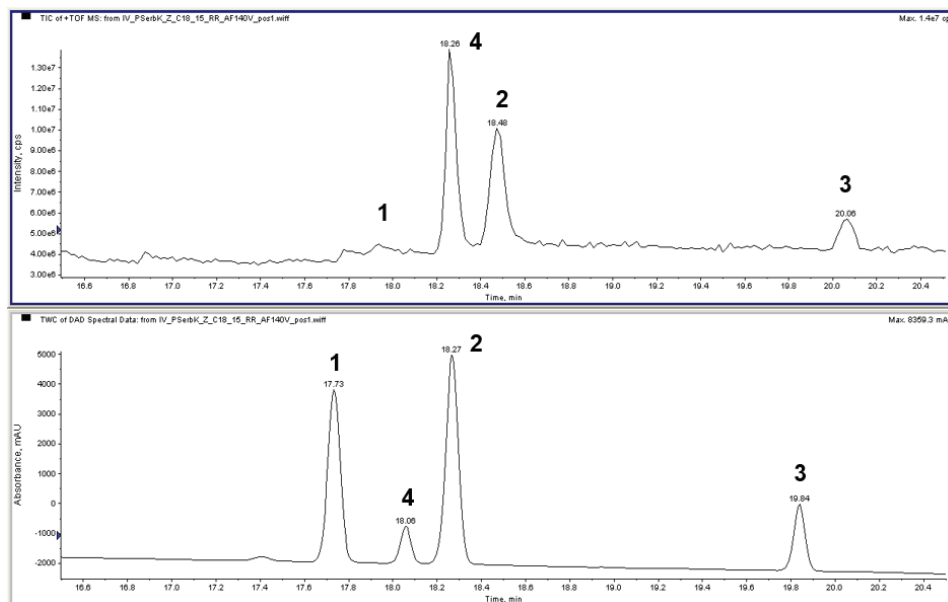


Fig. S-1. LC-MS (top) and LC-DAD (bottom) chromatogram of *P. serbica* root extract.

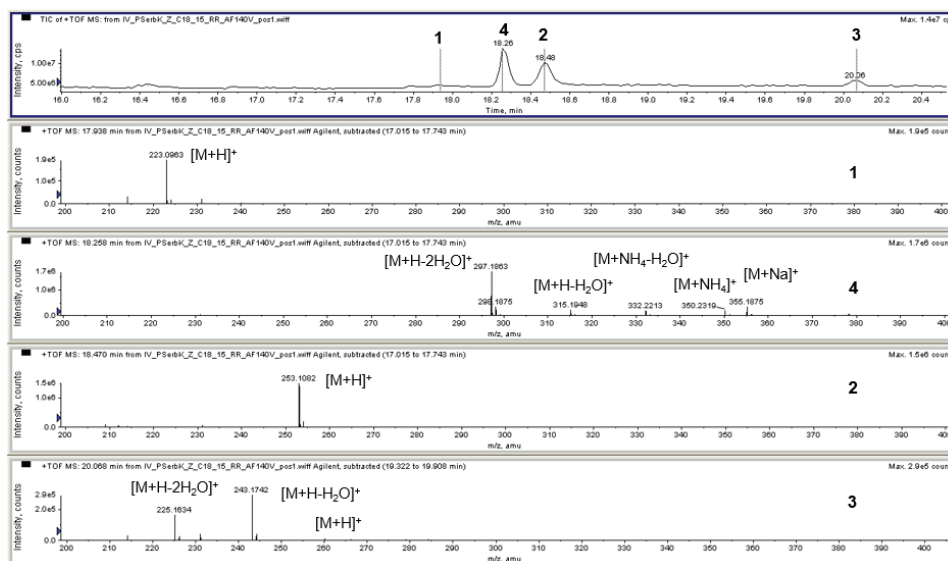


Fig. S-2. LC-MS chromatogram of *P. serbica* root extract and (+)ESI-HRMS spectra of compounds 1–4.

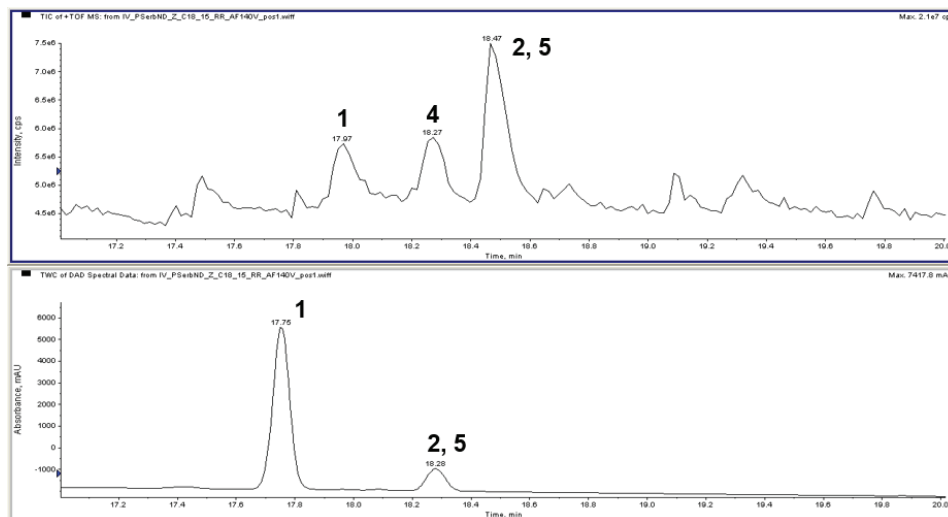


Fig. S-3. LC-MS (top) and LC-DAD (bottom) chromatogram of *P. serbica* aerial parts extract.

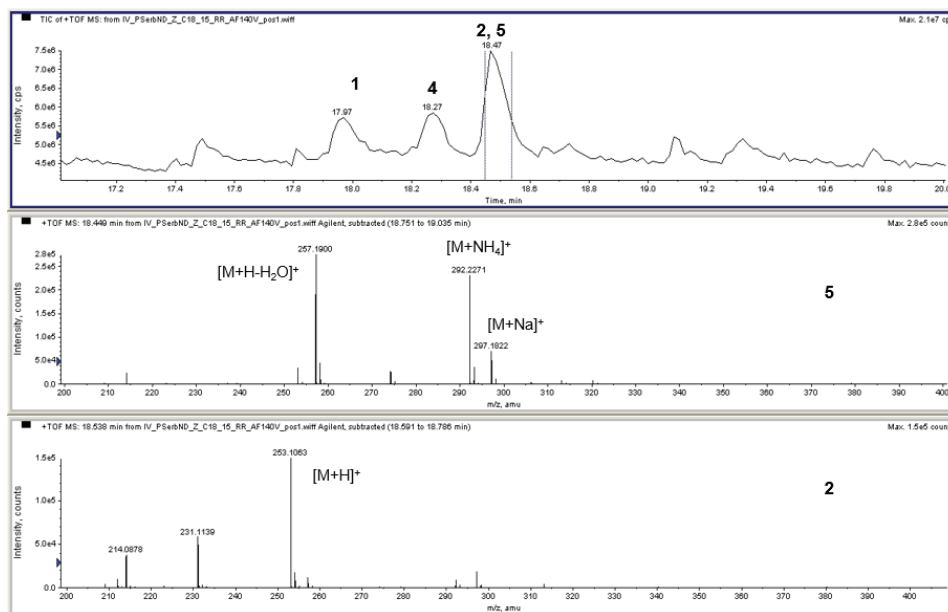


Fig. S-4. LC-MS chromatogram of *P. serbica* aerial parts extract and (+)ESI-HRMS spectra of compounds 2 and 5.

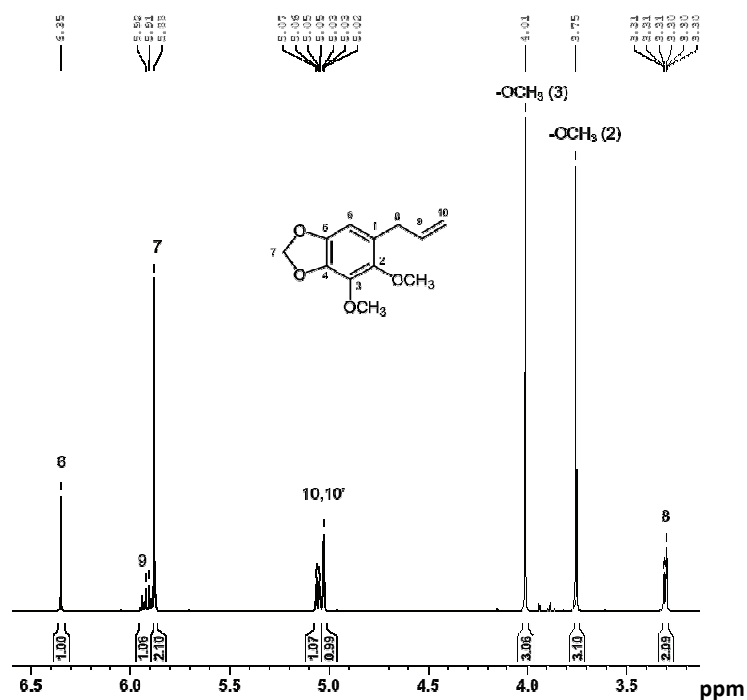


Fig. S-5. ¹H-NMR spectrum of compound 1 – dillapiolide (500 MHz, CDCl₃).

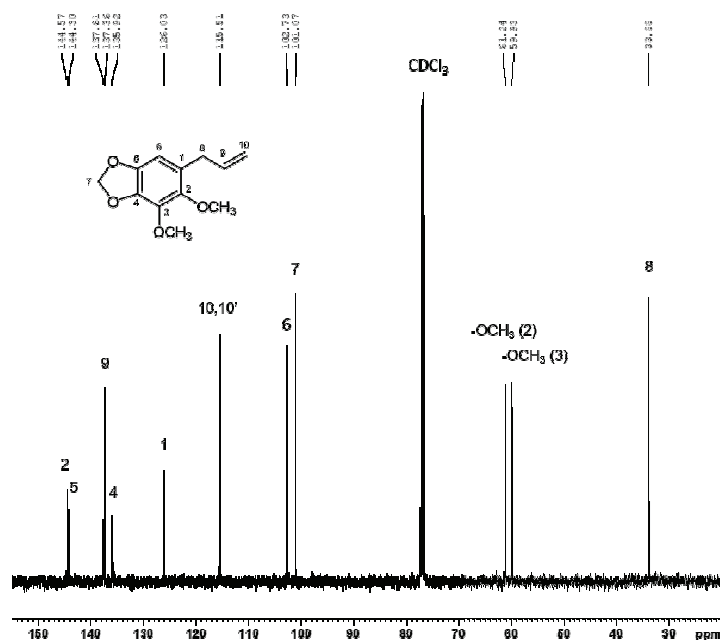


Fig. S-6. ¹³C-NMR spectrum of compound 1 – dillapiolide (125 MHz, CDCl₃).

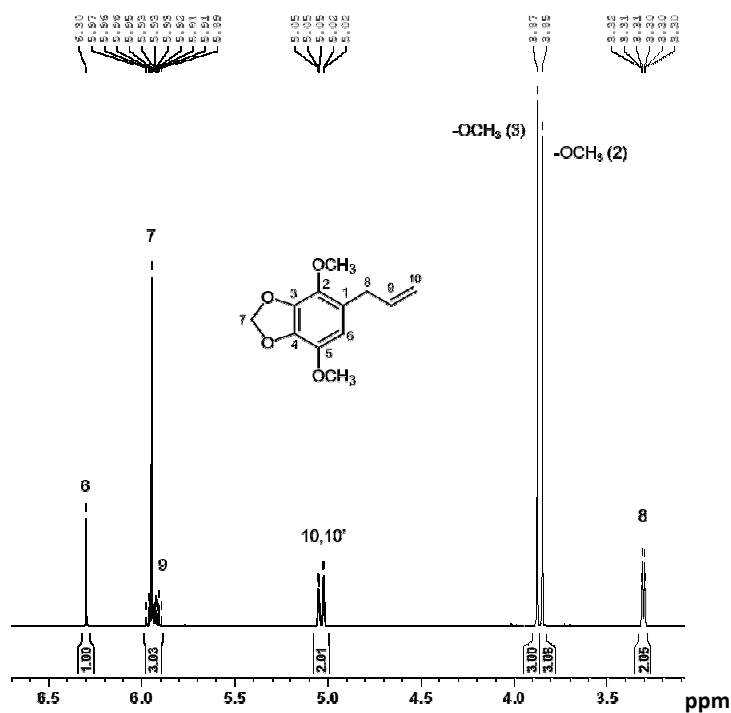


Fig. S-7. ^1H -NMR spectrum of apiole isolated from *Malabaila aurea* (500 MHz, CDCl_3).

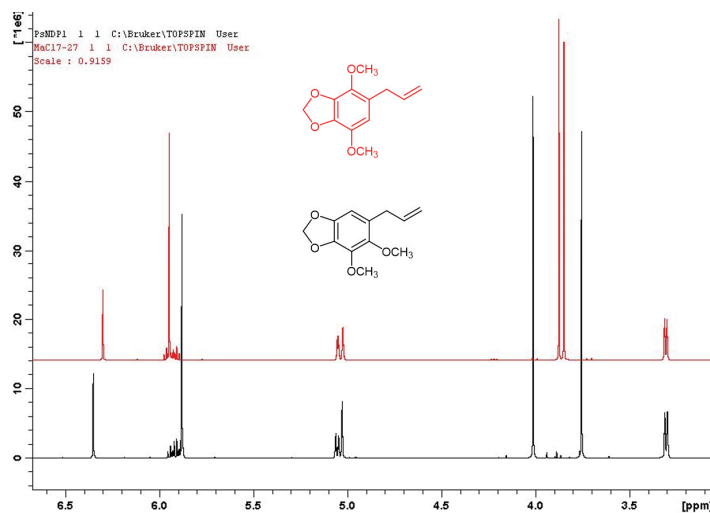


Fig. S-8. A comparison between the ^1H -NMR spectra of dillapiole from *Pimpinella serbica* and apiole from *Malabaila aurea*.

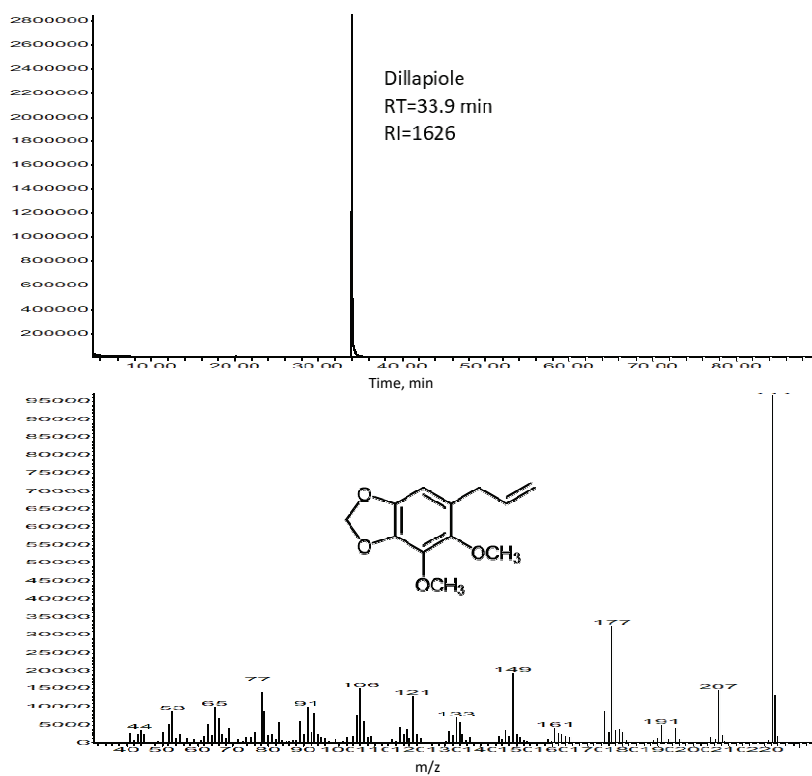


Fig. S-9. GC-MS chromatogram (top) and EI MS spectrum (bottom) of compound **1** - dillapiole.

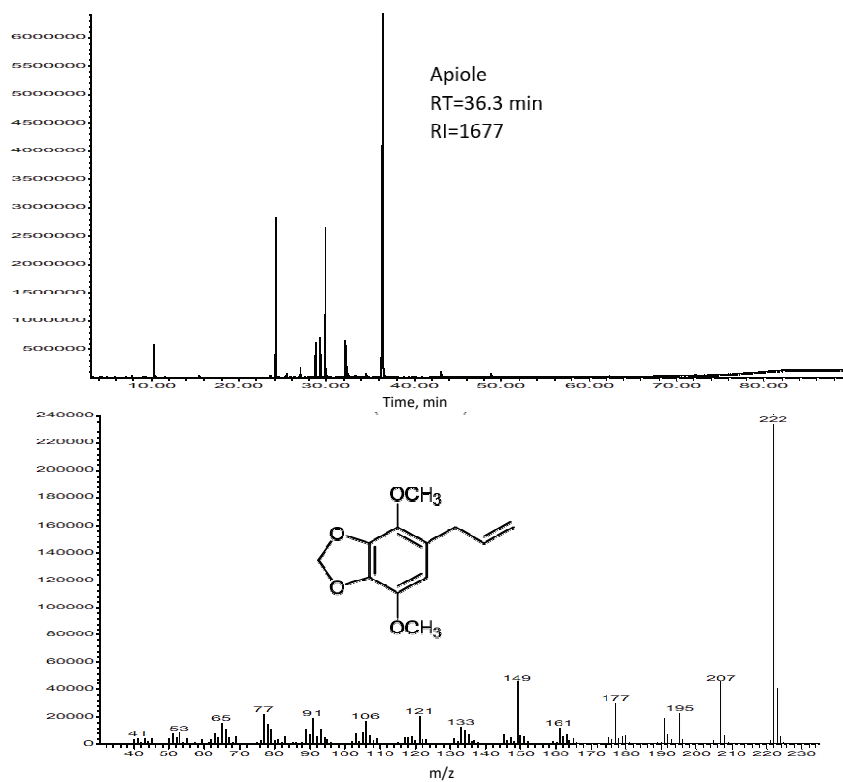


Fig. S-10. GC-MS chromatogram of *Malabaila aurea* essential oil (top) and EI MS spectrum of its major component apiole (bottom).

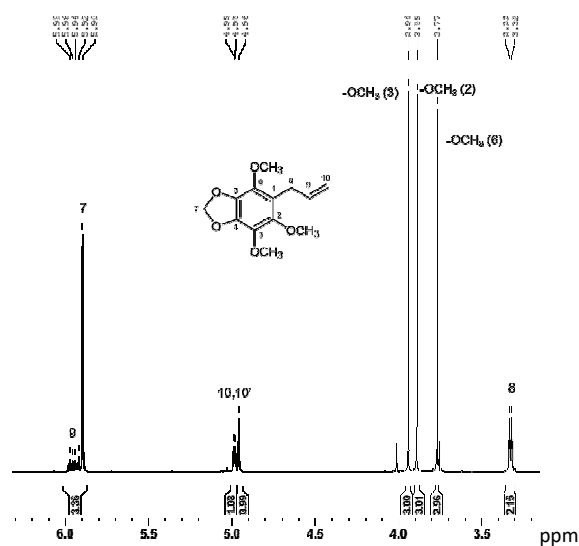
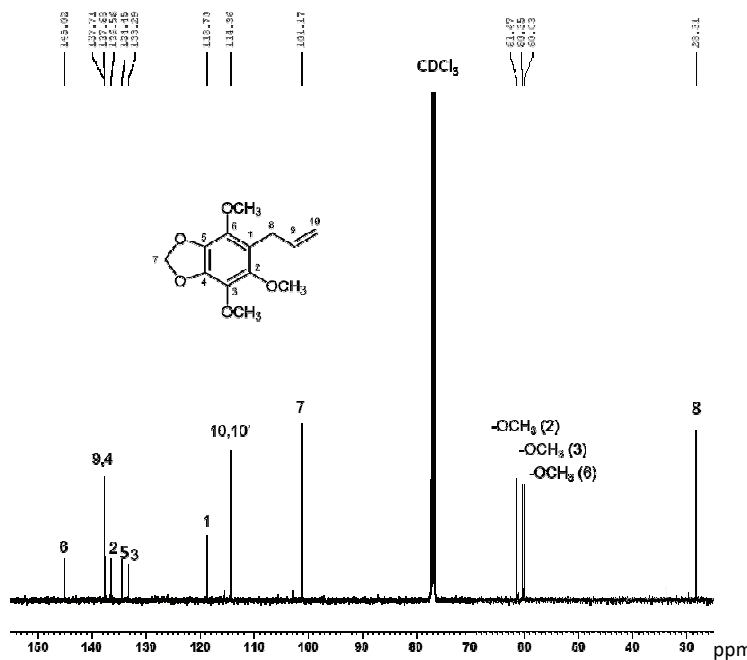


Fig. S-11. ¹H-NMR spectrum of compound 2 – nothoapiole (500 MHz, CDCl₃).



Fig' S-12. ¹³C-NMR spectrum of compound 2 – nothoapiole (125 MHz, CDCl₃).

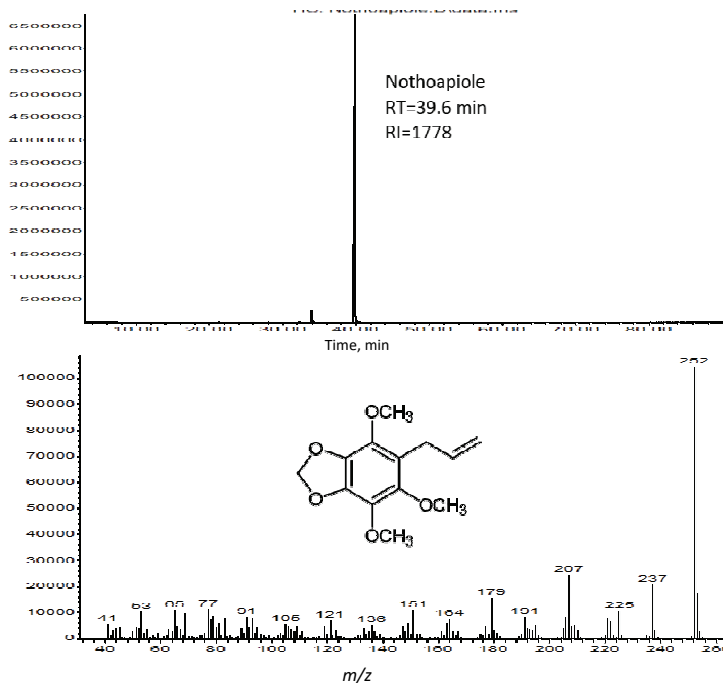


Fig. S 13. GC-MS chromatogram (top) and EI MS spectrum (bottom) of compound 2 (nothoapiole).

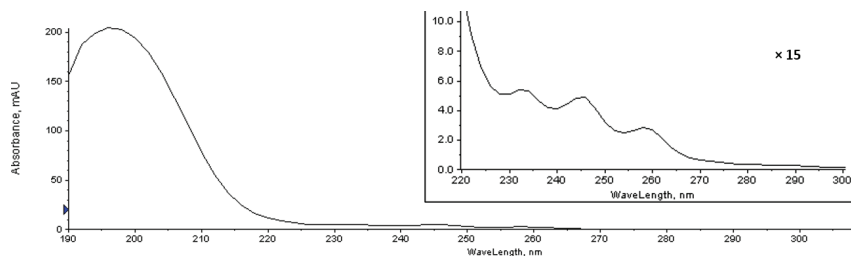
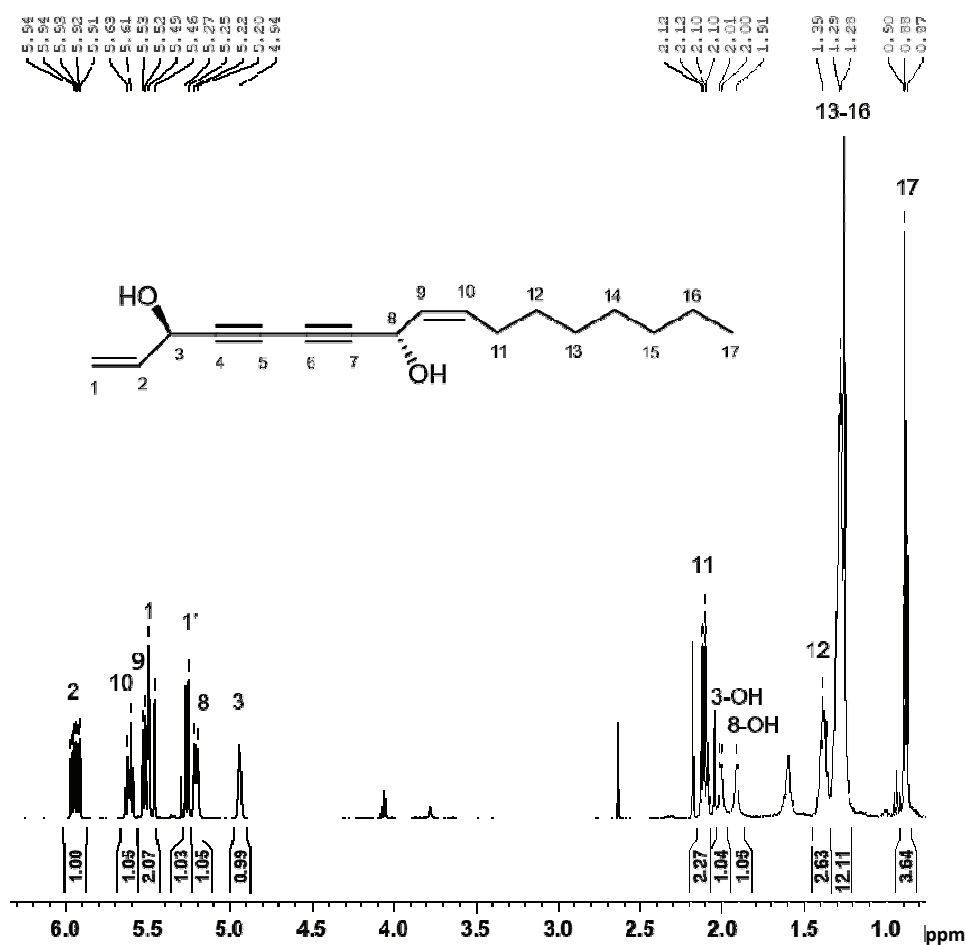


Fig. S 14. UV spectrum of compound 3 – falcarindiol.

Fig. S-15. $^1\text{H-NMR}$ spectrum of compound 3 – falcarindiol (500 MHz, CDCl_3).

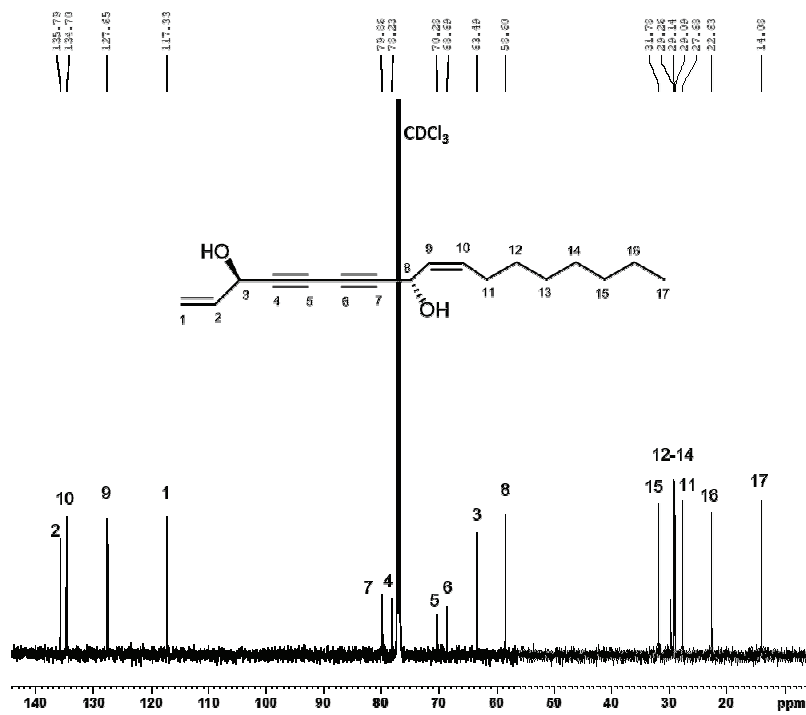


Fig. S-16. ¹³C-NMR spectrum of compound 3 – faltarindiol (125 MHz, CDCl₃).

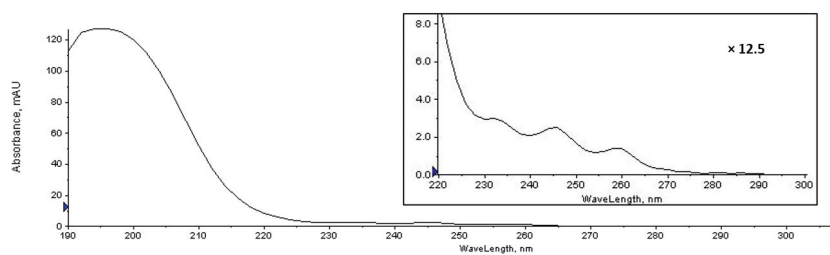
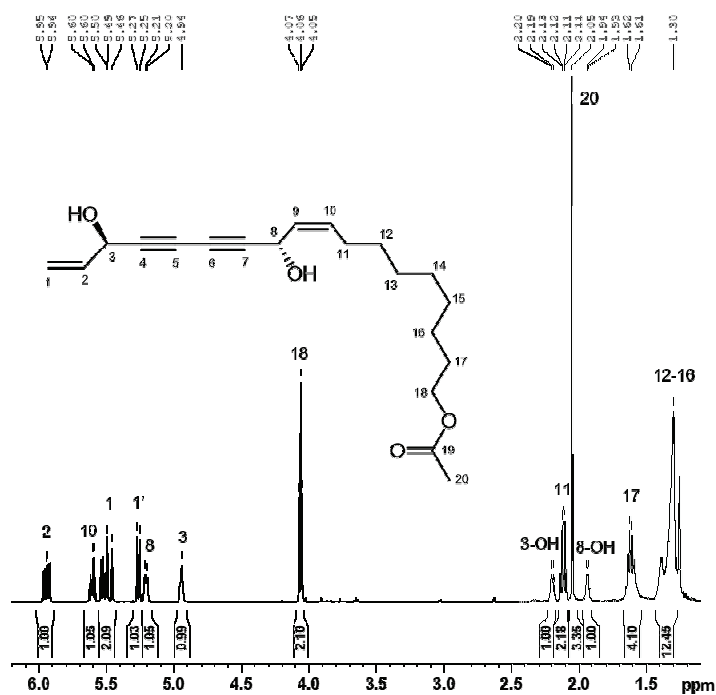
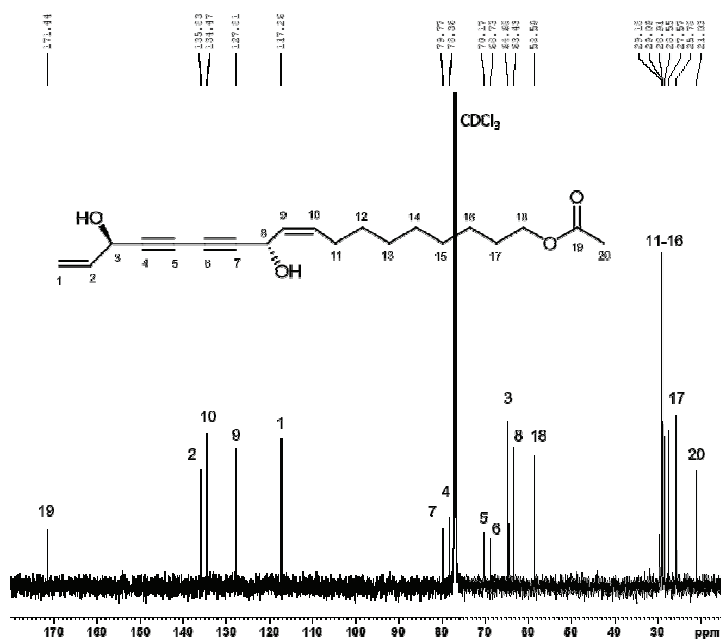
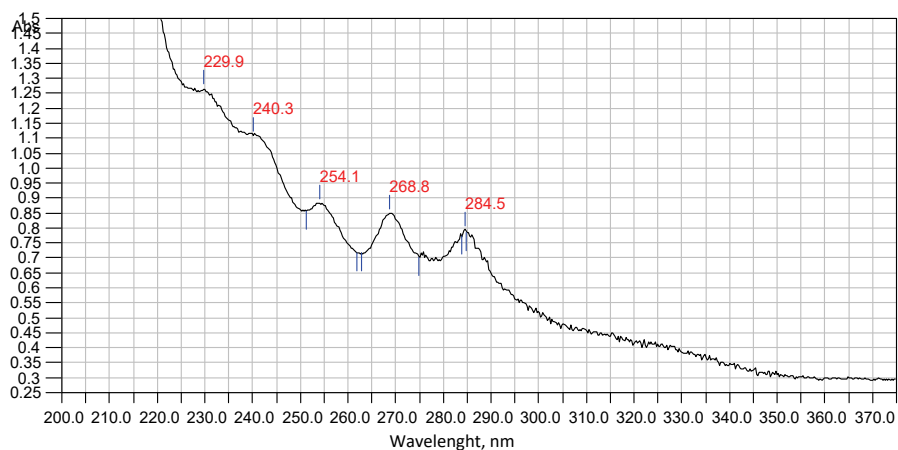


Fig. S-17. UV spectrum of compound 4 – oplopantriol A 18-acetate.

Fig. S-18. ¹H-NMR spectrum of compound 4 – oplanantriol A 18-acetate (500 MHz, CDCl₃).Fig.S-19. ¹³C-NMR spectrum of compound 4 – oplanantriol A 18-acetate (125 MHz, CDCl₃).



Fig; S-20. UV spectrum of compound 5 – dendrotrifidiol.

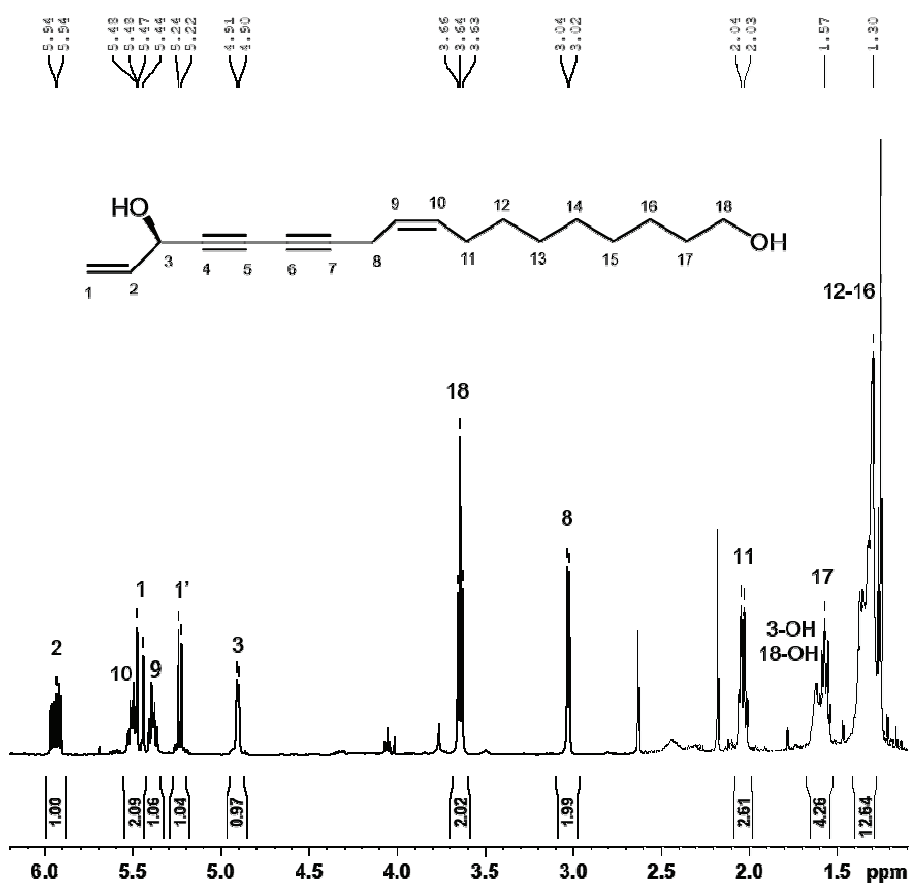


Fig. S-21. ¹H-NMR spectrum of compound 5 – dendrotrifidiol (500 MHz, CDCl₃).

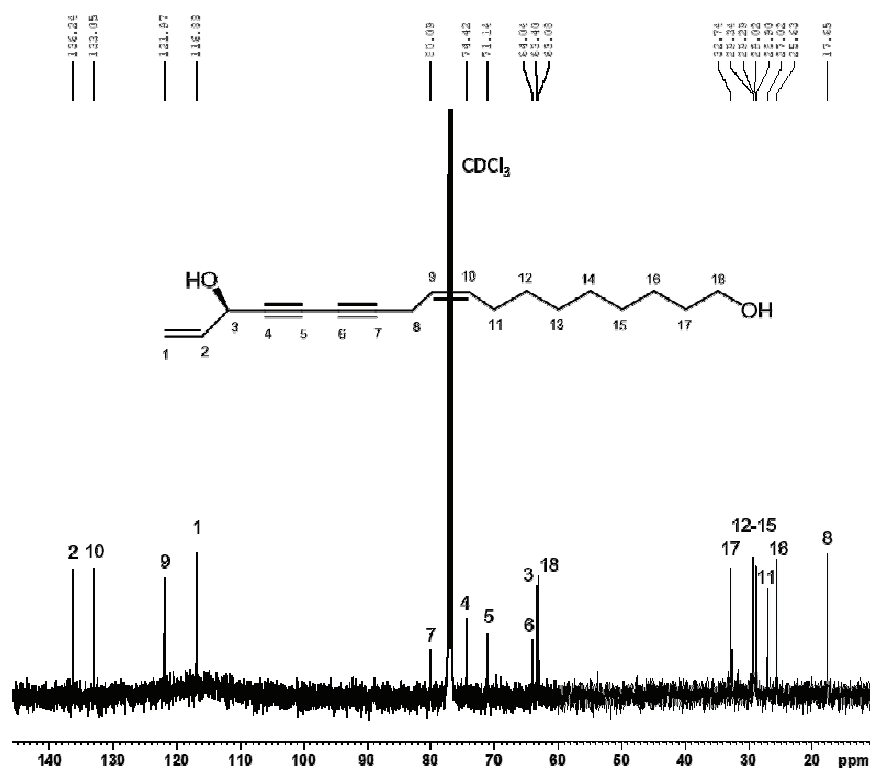


Fig. S-22. ^{13}C -NMR spectrum of compound 5 – dendrotrifidiol (125 MHz, CDCl_3).