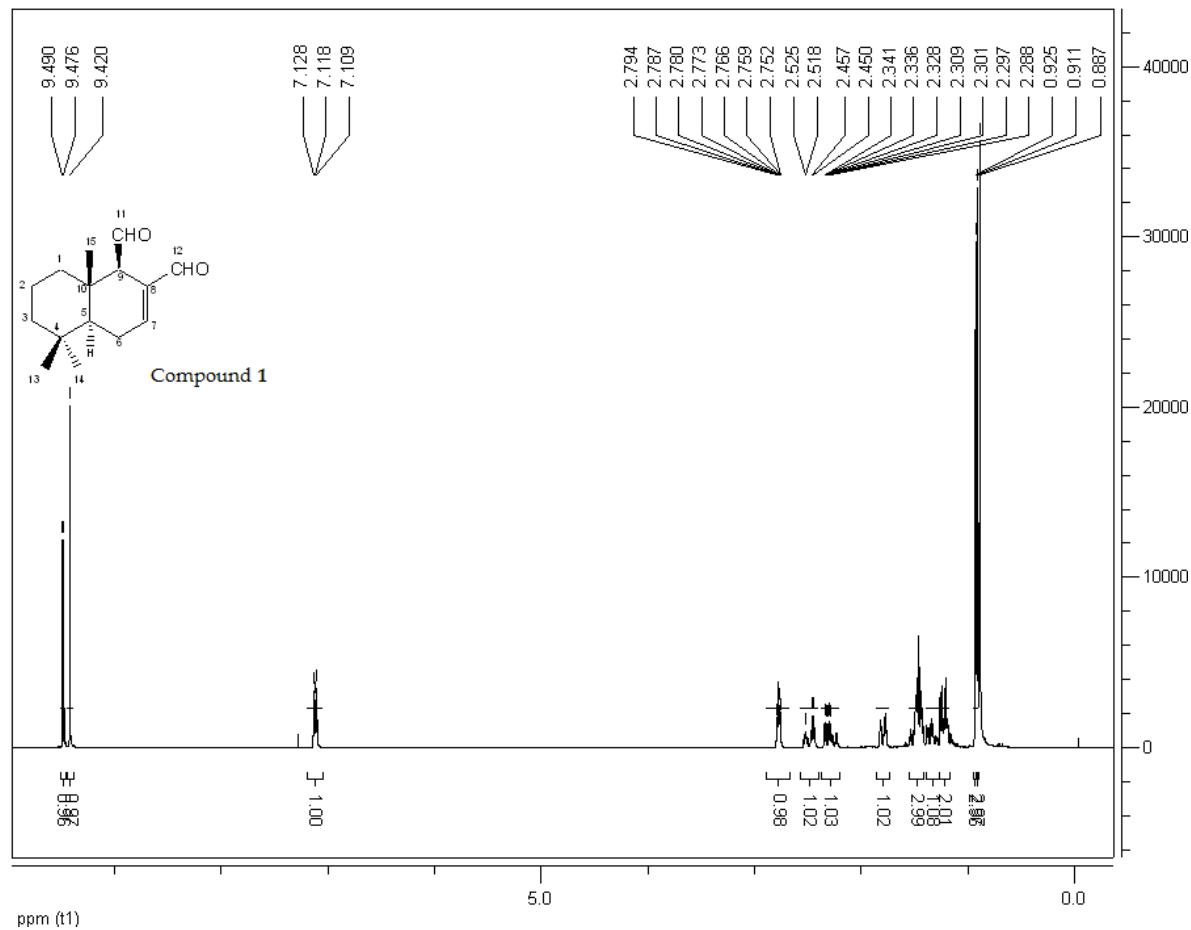


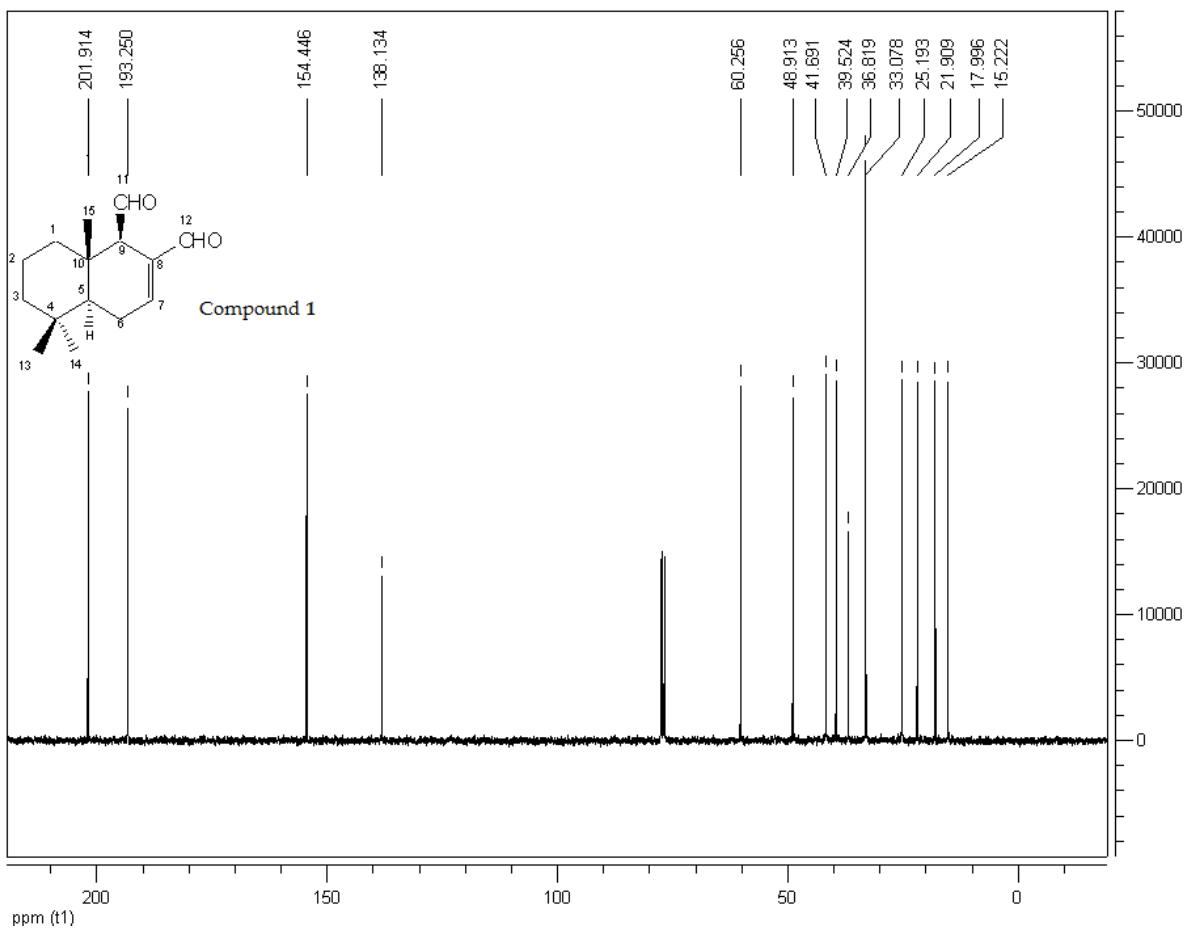
*Supplementary material.*

**1. Compound descriptions including  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra.**

Compound 1: MP: 48°C.  $[\alpha]_D$ : -27° ( $c$  1.00,  $\text{CHCl}_3$ ). IR (KBr): 2927, 2850, 2726, 1722, 1680, 1642,  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 9.48 (1H, *d*,  $J$ = 4.2 Hz, H-11); 9.42 (1H, *s*, H-12); 7.11 (1H, *m*, H-7); 2.78 (1H, *dd*<sub>4</sub>,  $J$ = 6.2, 2.1, 2.1 Hz, H-9); 2.55-2.40 (1H, *m*, H-6 $\alpha$ ); 2.35-2.20 (1H, *m*, H-6 $\beta$ ); 1.82 (1H, *m*, H-1 $\beta$ ); 1.54-1.43 (3H, *m*, H-2 $\alpha$ , 2 $\beta$ , 3 $\beta$ ); 1.34 (1H, *td*,  $J$ = 4.0 and 13.4 Hz, H-1 $\alpha$ ); 1.26-1.16 (2H, *m*, H-3 $\alpha$ , H-5); 0.92; (3H, *s*, Me-15); 0.91 and 0.89 (6H, 2s, Me-14 and Me-15).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 201.9 (HC=O); 193.2 (HC=O); 154.4 (=CH); 138.1 (=C); 60.2 (CH); 48.8 (CH); 41.7 (CH<sub>2</sub>); 39.5 (CH<sub>2</sub>); 36.8 (C); 33.0 (C); 33.0 (CH<sub>3</sub>); 25.1 (CH<sub>2</sub>); 21.9 (CH<sub>3</sub>); 17.9 (CH<sub>2</sub>); 15.2 (CH<sub>3</sub>). MS (EI, 70 eV):  $m/z$  (%) = 234 [M<sup>+</sup>], 216 [M<sup>+</sup> - H<sub>2</sub>O], 206 [M<sup>+</sup> - CO], 191 [206 - Me].

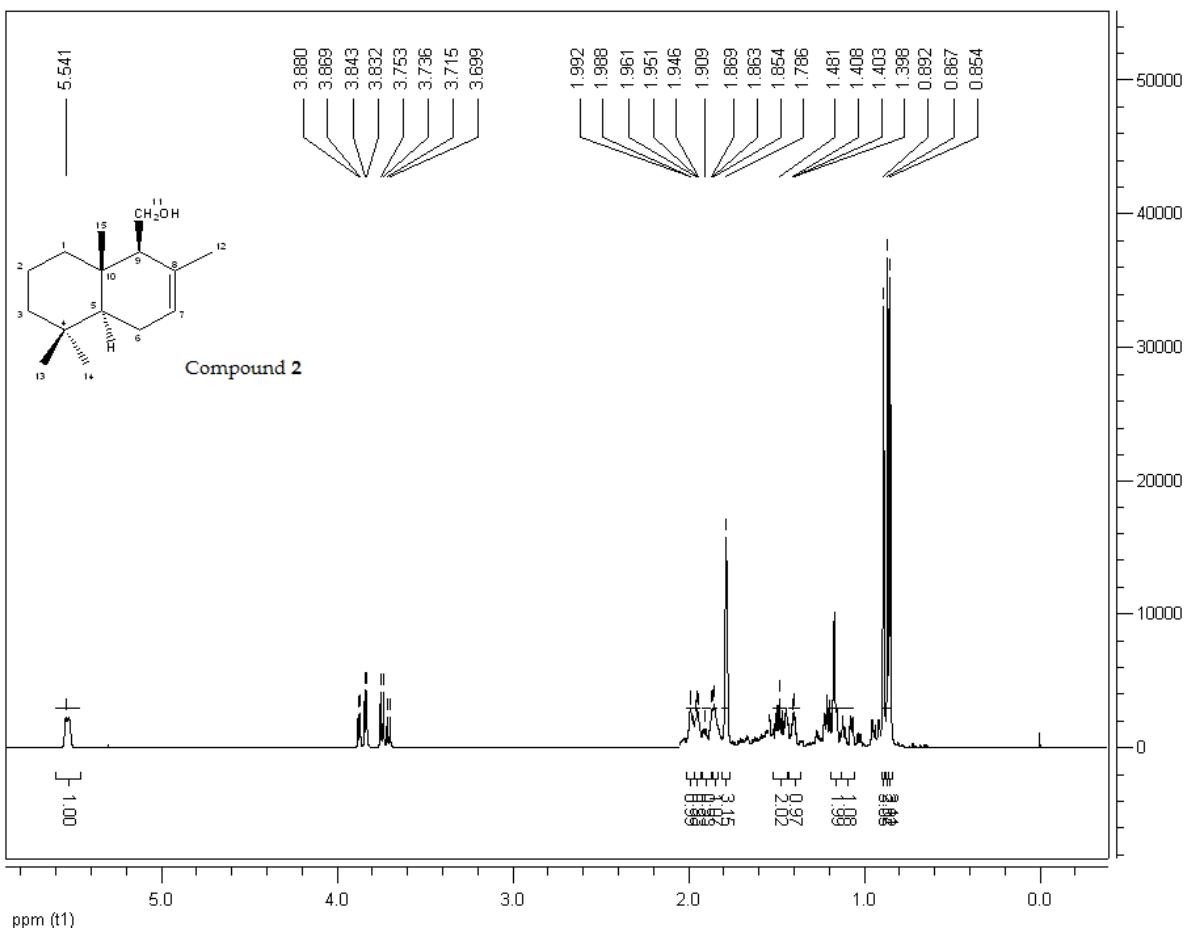


**Figure S1:**  $^1\text{H}$  NMR spectra of polygodial (1).

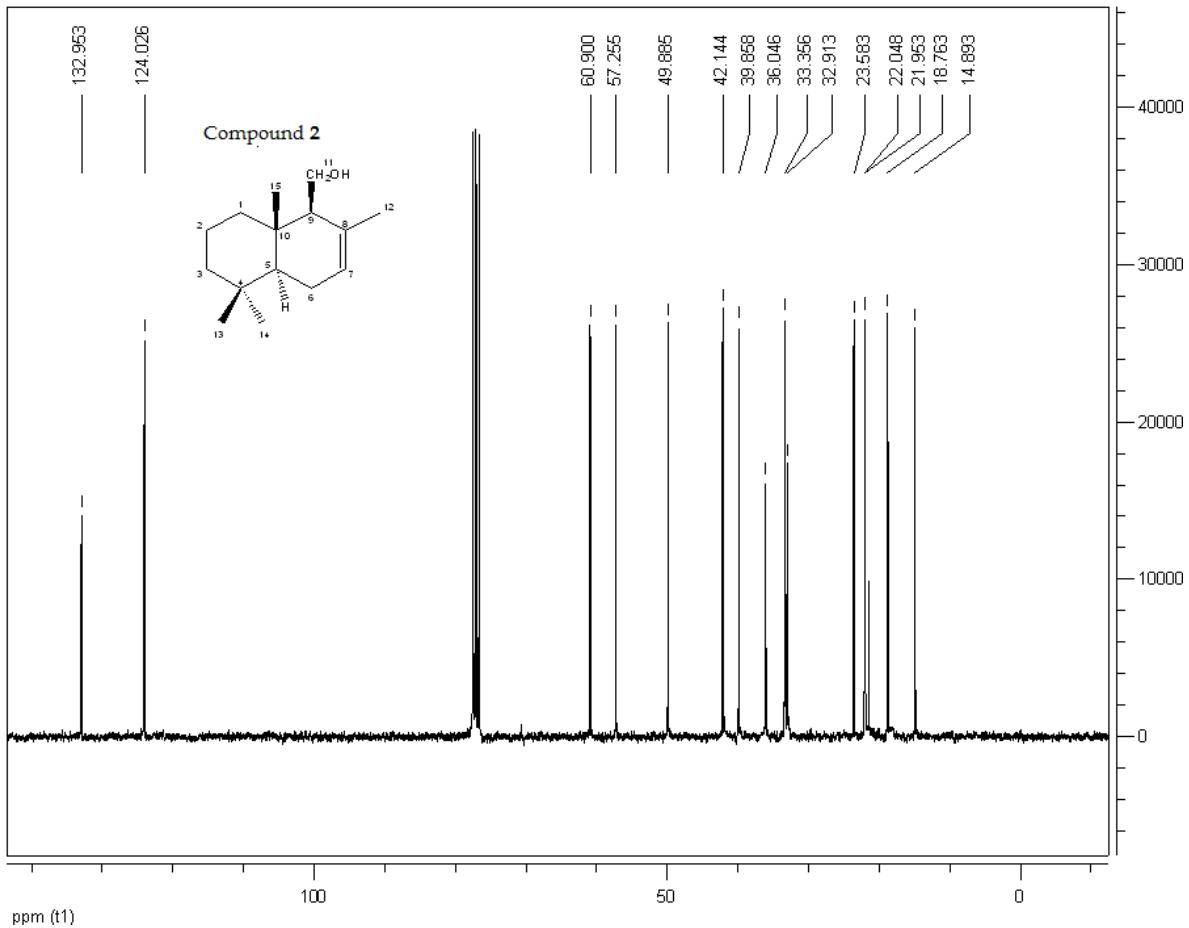


**Figure S2:** <sup>13</sup>C NMR spectra of polygodial (**1**).

Compound **2**: MP: 98°C.  $[\alpha]_D$ : -15° (c 1.00, CHCl<sub>3</sub>). IR (KBr): 3405, 2922, 1620 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 5.54 (1H, *m*, H-7); 3.85 (1H, *dd*, *J*= 3.3, 11.3 Hz, H-11B); 3.73 (1H, *dd*, *J*= 3.3, 11.3 Hz, H-11A); 1.97 (1H, *m*, H-6 $\alpha$ ); 1.95 (1H, *m*, H-1 $\beta$ ); 1.92 (1H, *m*, H-6 $\beta$ ); 1.86 (1H, *m*, H-9); 1.79 (3H, *s*, Me-12); 1.48 (2H, *m*, H-2 $\alpha$  and 2 $\beta$ ); 1.41 (1H, *m*, H-3 $\beta$ ); 1.20 (2H, *m*, H-3 $\alpha$  and H-5); 1.07 (1H, *m*, H-1 $\alpha$ ); 0.89, 0.87 and 0.85 (9H, 3*s*, Me-13, 14 and 15). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 132.9 (=C); 124.0 (=CH); 60.9 (H<sub>2</sub>C-OH); 57.3 (CH); 49.9 (CH); 42.1 (CH<sub>2</sub>); 39.8 (CH<sub>2</sub>); 36.0 (C); 33.3 (CH<sub>3</sub>); 32.9 (C); 23.6 (CH<sub>2</sub>); 22.0 (CH<sub>3</sub>); 21.9 (CH<sub>3</sub>); 21.9 (CH<sub>3</sub>); 18.8 (CH<sub>2</sub>); 14.9 (CH<sub>3</sub>). MS (EI, 70 eV): m/z (%) = 234 [M<sup>+</sup>], 216 [M<sup>+</sup> - H<sub>2</sub>O], 206 [M<sup>+</sup> - CO], 191 [206 - Me].

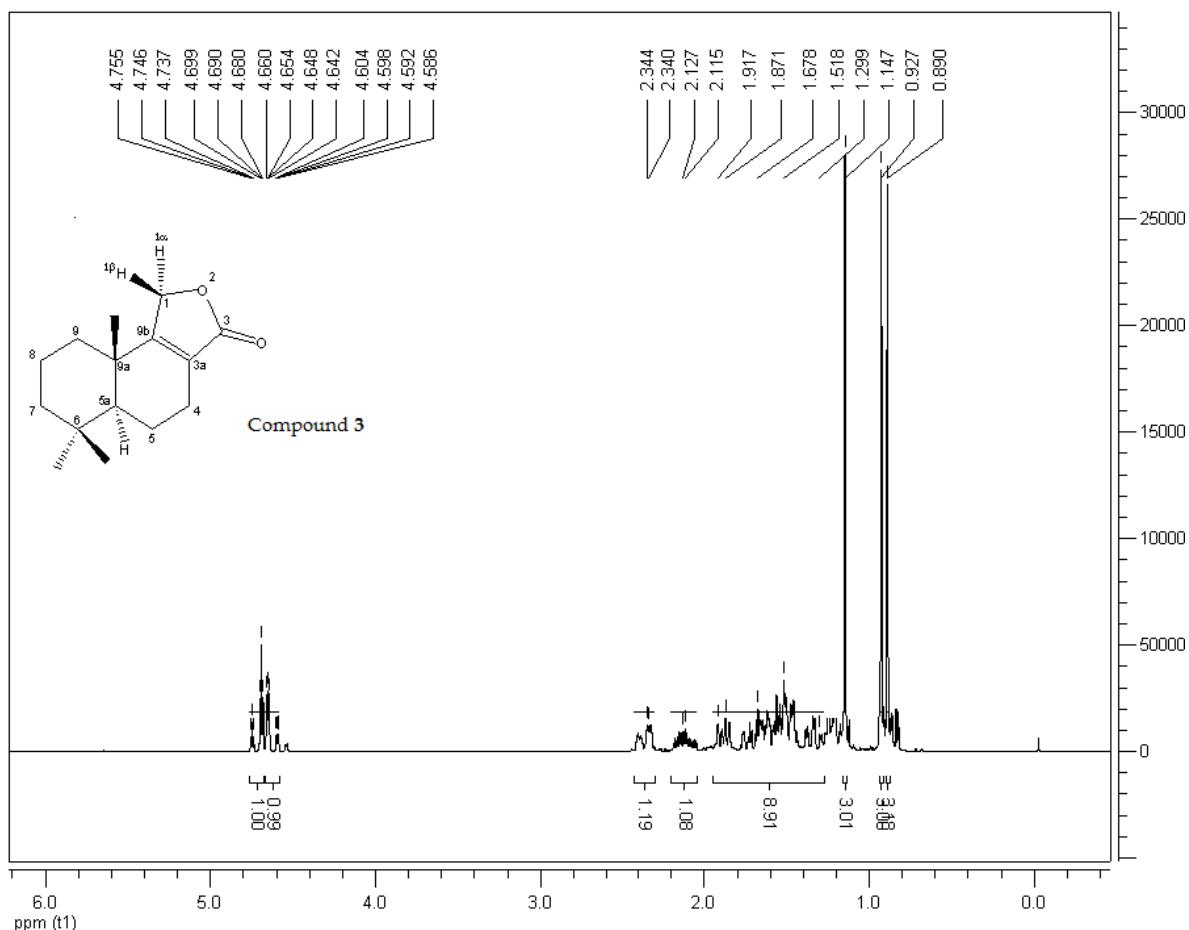


**Figure S3:** <sup>1</sup>H NMR spectra of drimenol (2).

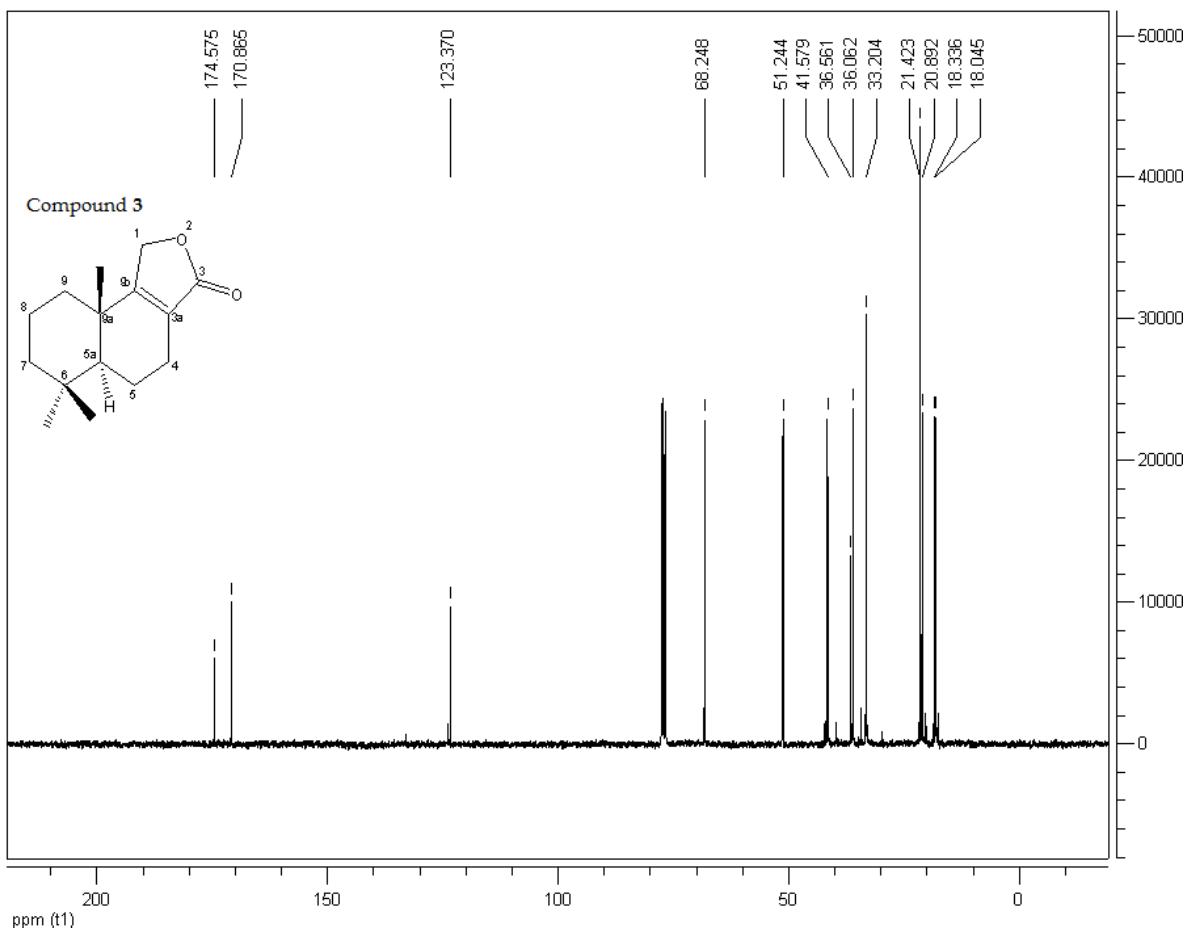


**Figure S4:**  $^{13}\text{C}$  NMR spectra of drimenol (2).

Compound 3: MP: 153°C.  $[\alpha]_D$ : +70° (*c* 1.00,  $\text{CHCl}_3$ ). IR (KBr): 1769, 1677  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 4.72 (1H, *ddd*, *J*=2.8, 2.8, 16.9 Hz, H-1 $\alpha$ ); 4.62 (1H, *ddd*, *J*=1.7, 3.5, 16.9 Hz, H-1 $\beta$ ); 2.54-2.05 (2H, *m*, H-4 $\alpha$  and  $\beta$ ); 1.92-1.30 (9H, *m*, H-5 $\alpha$  and  $\beta$ , H-5a, H-7 $\alpha$  and  $\beta$ , H-8 $\alpha$  and  $\beta$ , H-9 $\alpha$  and  $\beta$ ); 1.15 (3H, *s*, Me-9a); 0.93 and 0.89 (6H, 2s, Me-6 $\alpha$  and  $\beta$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 174.5 (C=O); 170.8 (=C); 123.4 (=C); 68.2 ( $\text{CH}_2$ ); 51.2 ( $\text{CH}$ ); 41.6 ( $\text{CH}_2$ ); 36.6 ( $\text{CH}_2$ ); 36.0 (C); 33.2 (C); 33.2 ( $\text{CH}_3$ ); 21.4 ( $\text{CH}_2$ ); 21.4 ( $\text{CH}_3$ ); 20.9 ( $\text{CH}_3$ ); 18.3 ( $\text{CH}_2$ ); 18.0 ( $\text{CH}_2$ ). MS (EI, 70 eV): m/z (%) = 234 [ $\text{M}^+$ ], 216 [ $\text{M}^+ - \text{H}_2\text{O}$ ], 206 [ $\text{M}^+ - \text{CO}$ ], 191 [206 - Me].

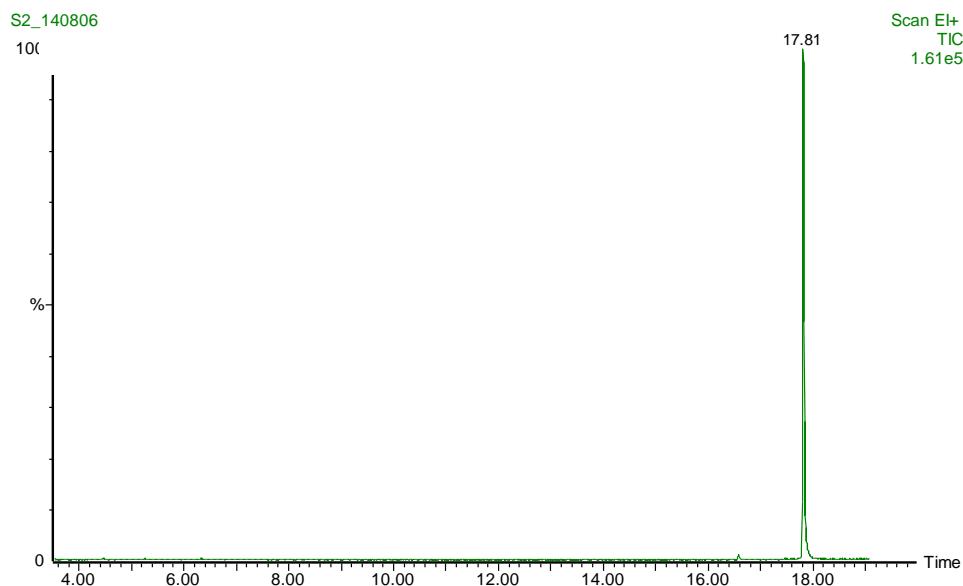


**Figure S5:**  $^1\text{H}$  NMR spectra of confertifolin (3).

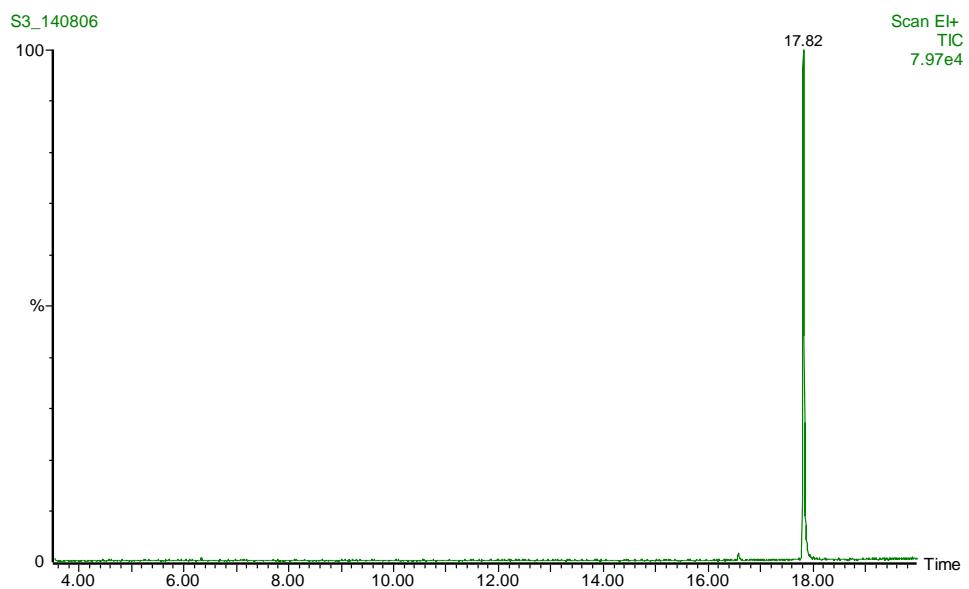


**Figure S6:** <sup>13</sup>C NMR spectra of confertifolin (3).

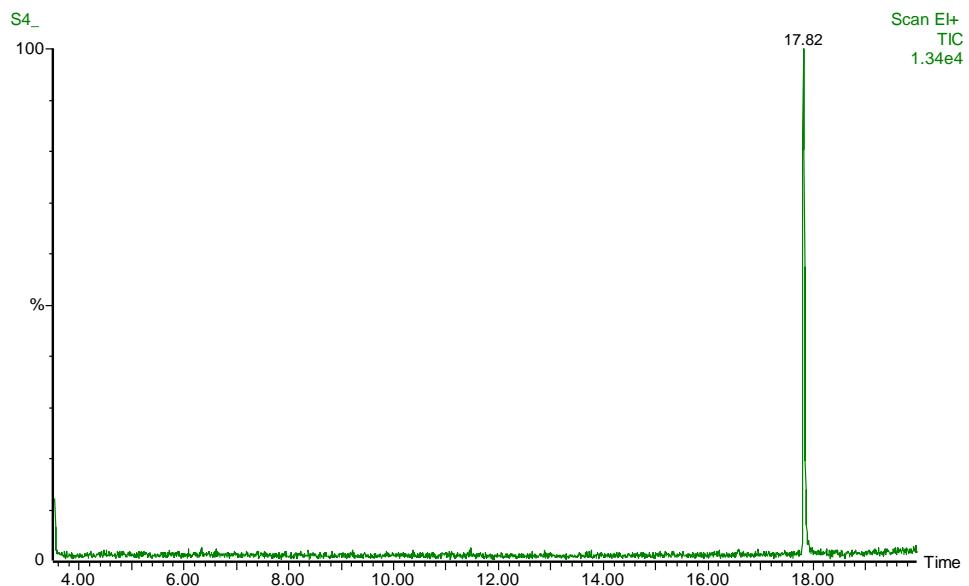
2. Gas chromatograms and Total Ion Chromatogram (TIC) areas obtained for different solution concentrations (0.5, 0.25 and 0.125 mg/mL) of pure polygodial and for EtOAc extract of *P. acuminata* (1 mg/mL). A mass spectrum is also showed.



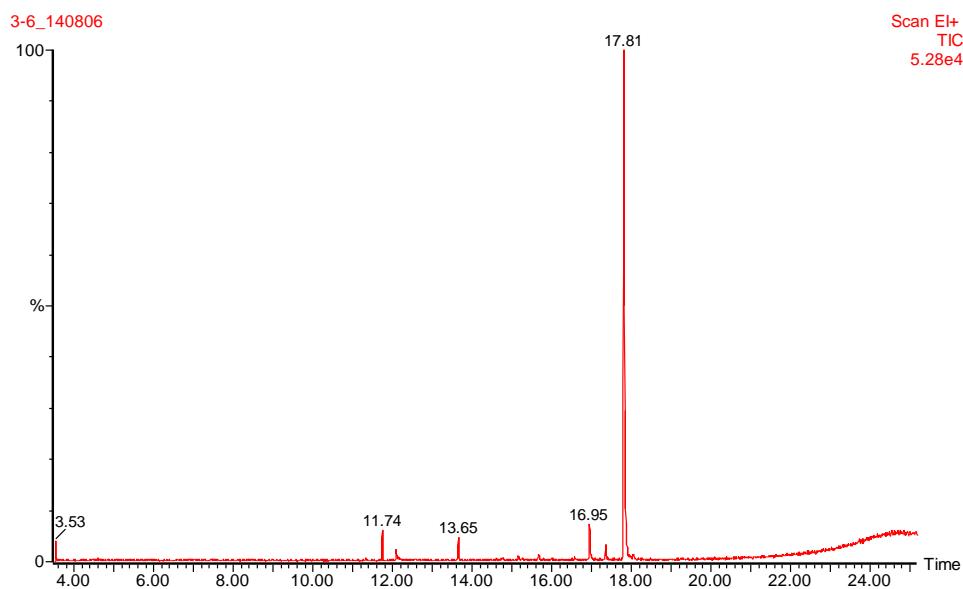
**Figure S7:** Gas chromatogram and Total Ion Chromatogram (TIC) area obtained for 0.5 mg/mL solution of polygodial (1).



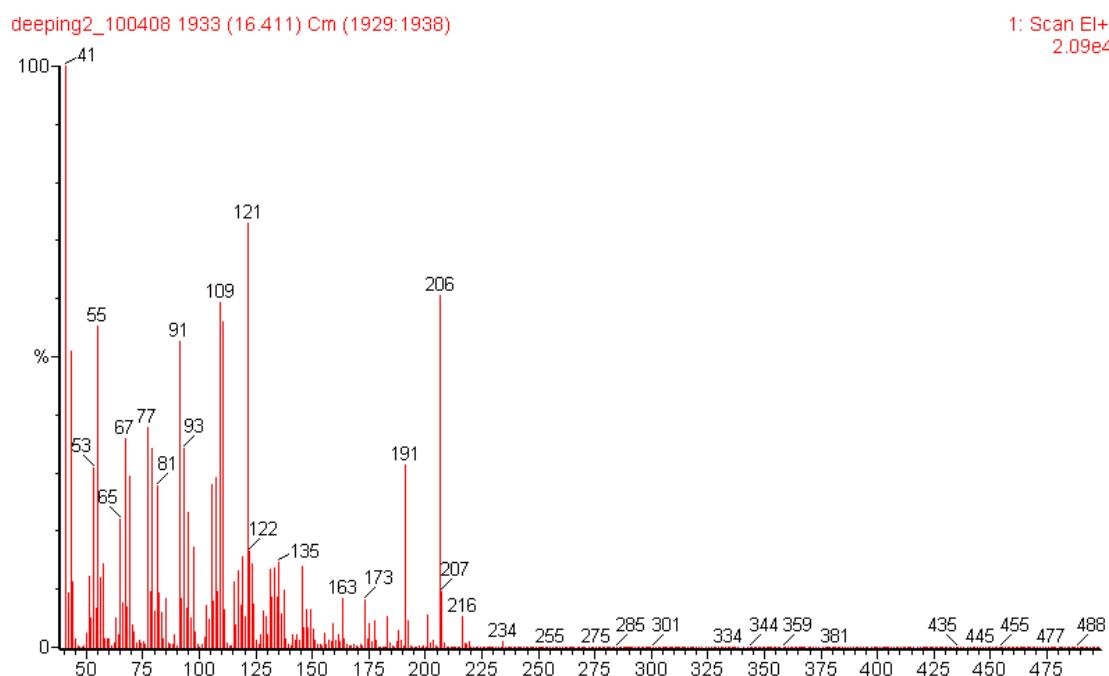
**Figure S8:** Gas chromatogram and Total Ion Chromatogram (TIC) area obtained for 0.25 mg/mL solution of polygodial (**1**).



**Figure S9:** Gas chromatogram and Total Ion Chromatogram (TIC) area obtained for 0.125 mg/mL solution of polygodial (**1**).



**Figure S10:** Gas chromatogram and Total Ion Chromatogram (TIC) area obtained for Ethyl Acetate extract of *P. acuminata* (1 mg/mL).



**Figure S11:** Mass spectrum of pure polygodial (1).