

# Supplementary Information

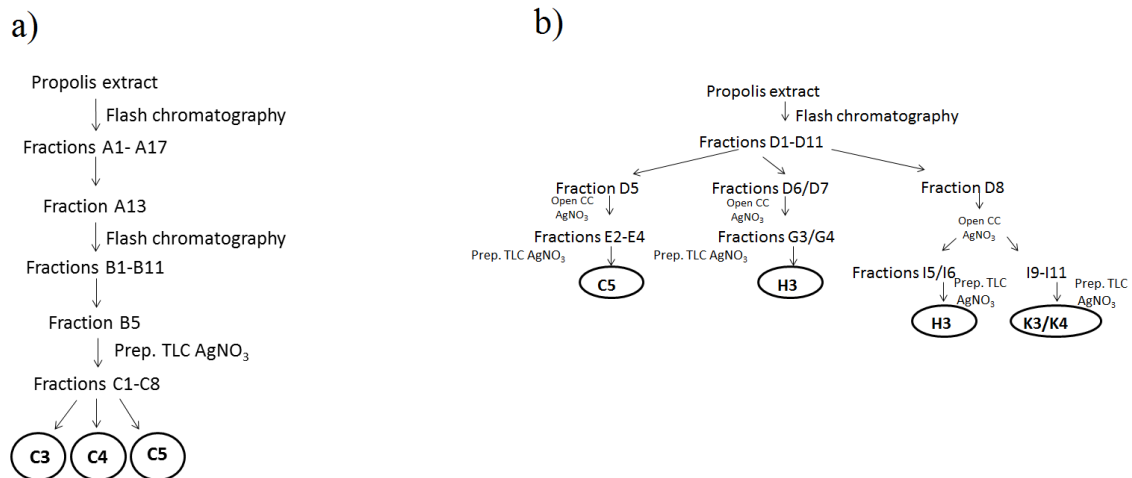
## Resorcinolic Lipids from Yucatecan Propolis

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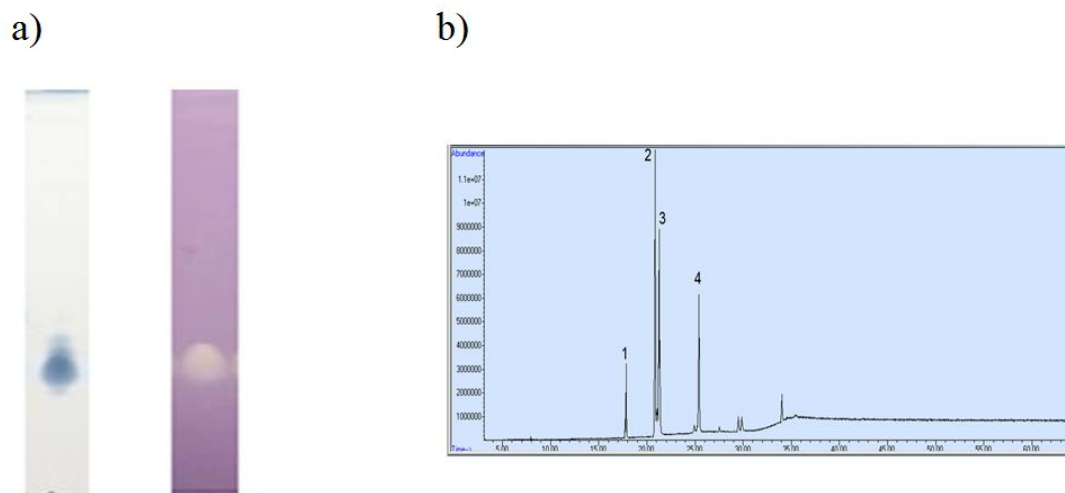
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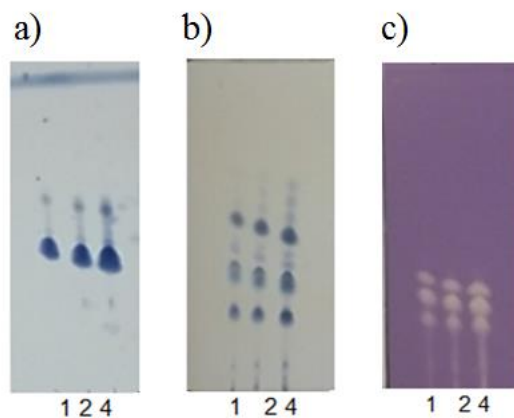
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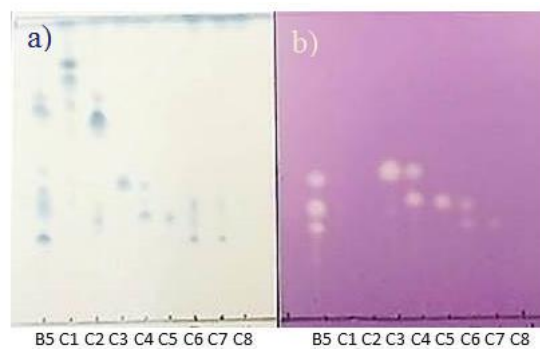
**Figure S1.** Chromatographic procedures used for the purification of the propolis extract.



**Figure S2.** (a) TLC chromatographic profile of fraction B5 visualized with phosphomolybdic acid reagent (left) and DPPH (right; metabolites with antioxidant activity appear as yellow spots on a purple background); (b) GC-MS chromatographic profile of fraction B5 showing four major components.



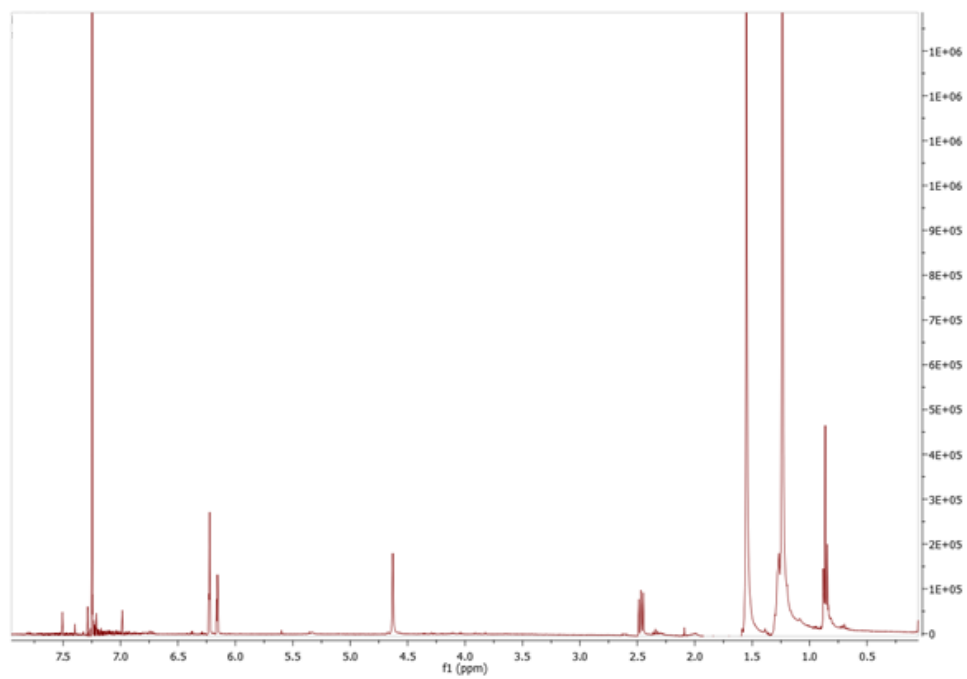
**Figure S3.** (a) TLC chromatographic profile of fraction B5 on a normal plate visualized with phosphomolybdic acid reagent; (b) TLC chromatographic profile of fraction B5 on a plate impregnated with silver nitrate, visualized with phosphomolybdic acid reagent; (c) TLC chromatographic profile of fraction B5 on a plate impregnated with silver nitrate, visualized with DPPH (metabolites with antioxidant activity appear as yellow spots on a purple background).



**Figure S4.** Fractions obtained after prep TLC purification of fraction B5 using AgNO<sub>3</sub>-impregnated silica gel plates; analytical TLC plates impregnated with AgNO<sub>3</sub> and visualized with phosphomolybdic acid reagent (a) and DPPH (b); metabolites with antioxidant activity appear as yellow spots on a purple background.

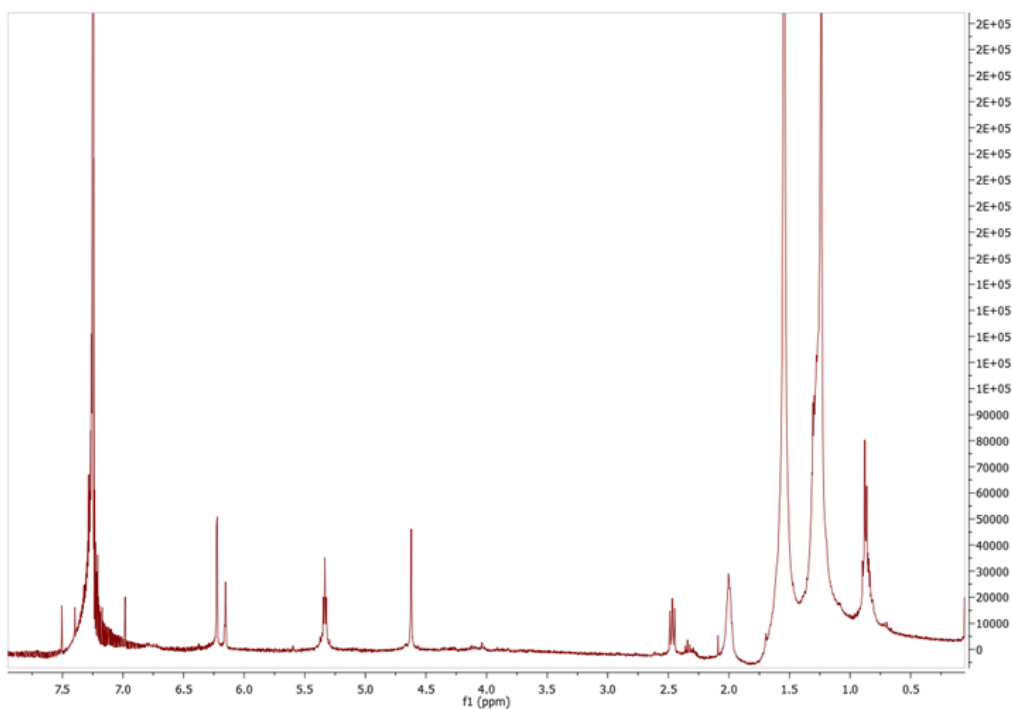
**Table S1.** <sup>1</sup>H NMR data of purified fractions C3-C5 and K4

Fraction	Metabolite	<sup>1</sup> H NMR data
Fraction C3	1,3-benzenediol-5-pentadecyl ( <b>1</b> ) and 1,3-benzenediol-5-heptadecyl ( <b>2</b> )	$\delta$ 0.87 (m, <u>CH</u> <sub>3</sub> ), 2.48 (t, <i>J</i> 7.9 Hz, H1'), 4.64 (s, <u>OH</u> ), 6.17 (t, <i>J</i> 2.3 Hz, H2), 6.24 (d, <i>J</i> 2.3 Hz, H4/H6)
Fraction C4	1,3-benzenediol-5-pentadecyl ( <b>1</b> ) and 1,3-benzenediol-5-(14-nonadecenyl) ( <b>4</b> )	$\delta$ 0.88 (m, <u>CH</u> <sub>3</sub> ), 1.99-2.02 (m, <u>-CH</u> <sub>2</sub> -CH=CH- <u>CH</u> <sub>2</sub> -), 2.50-2.45 (t, <i>J</i> 7.6 Hz, H1'), 4.64 (s, OH), 5.35 (m, <u>CH</u> = <u>CH</u> ), 6.17 (t, <i>J</i> 2.3 Hz, H2), 6.24 (d, <i>J</i> 2.3 Hz, H4/H6)
Fraction C5	1,3-benzenediol-5-(12-heptadecenyl) ( <b>3</b> ) and 1,3-benzenediol-5-(14-nonadecenyl) ( <b>4</b> )	$\delta$ 0.89 (m, <u>CH</u> <sub>3</sub> ), 1.99-2.03 (m, <u>-CH</u> <sub>2</sub> -CH=CH- <u>CH</u> <sub>2</sub> -), 2.46-2.51 (t, <i>J</i> 7.6 Hz, H1'), 4.64 (s, OH), 5.35 (m, <u>CH</u> = <u>CH</u> ), 6.17 (t, <i>J</i> 2.2 Hz, H2), 6.24 (d, <i>J</i> 2.3 Hz, H4/H6)
Fraction K4	1,3-benzenediol-5-(8,11-heptadecadienyl) ( <b>5</b> )	$\delta$ 0.89-0.87 (3H, m, H-17'), 1.32 (16H, <u>CH</u> <sub>2</sub> ), 2.05 (4H, dd, <i>J</i> 7.8, 7.3 Hz, H7/H13'), 2.48 (2H, t, <i>J</i> 7.8 Hz, H-1'), 2.77 (2H, t, <i>J</i> 7.2 Hz, H-10'), 5.35 (4H, m, H-8'/H-9'/H-11'/H-12'), 6.17 (1H, d, <i>J</i> 3.0 Hz, H-2), 6.24 (2H, t, <i>J</i> 1.8 Hz, H-4/H-6)

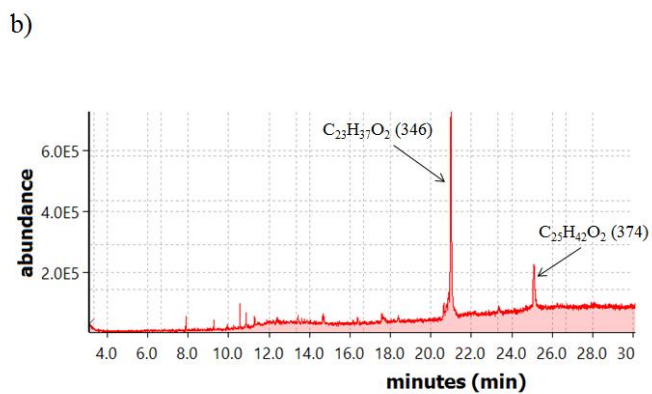
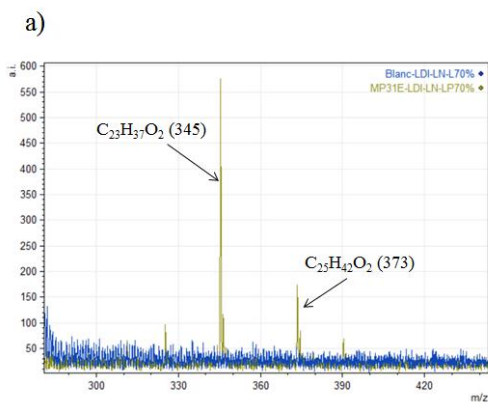


**Figure S5.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of purified fraction C3.



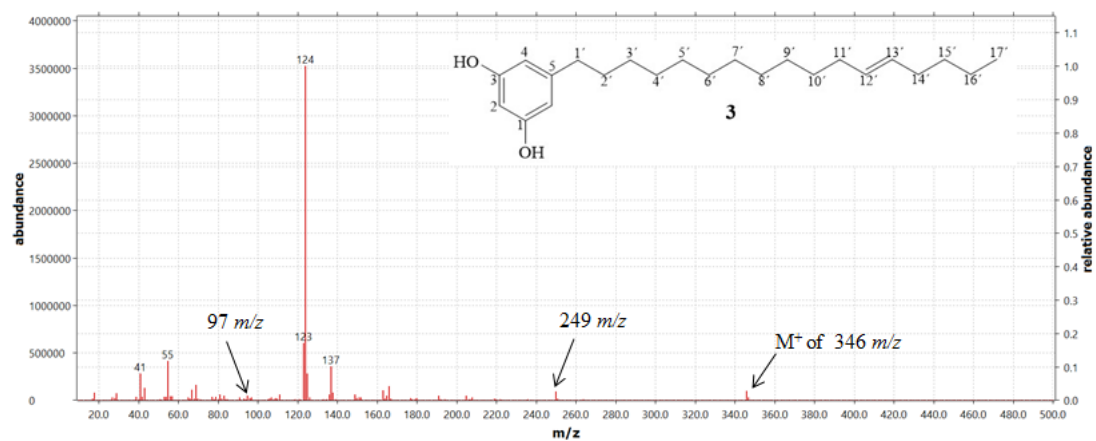


**Figure S8.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of purified fraction C5.

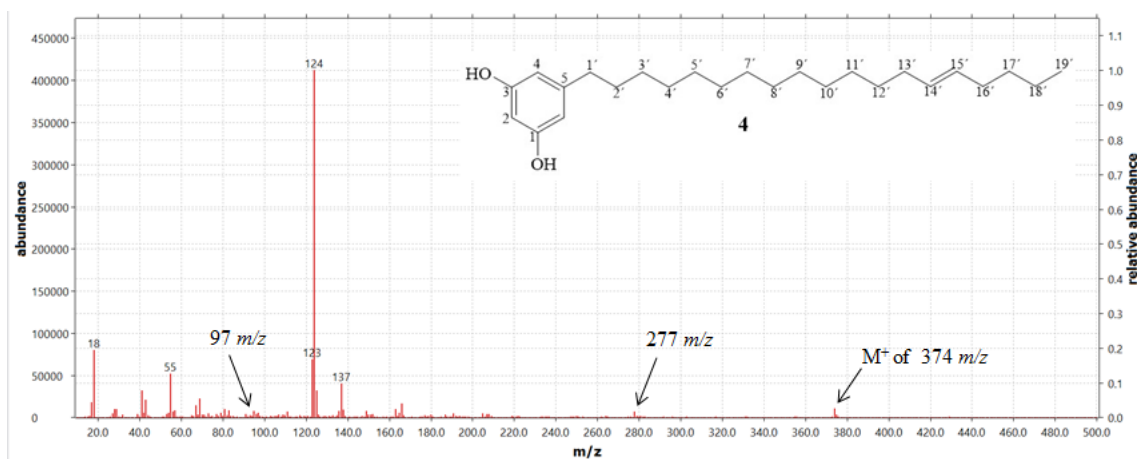


**Figure S9.** (a) LDI spectrum (negative mode) and (b) GC-MS chromatographic profile of purified fraction C5.

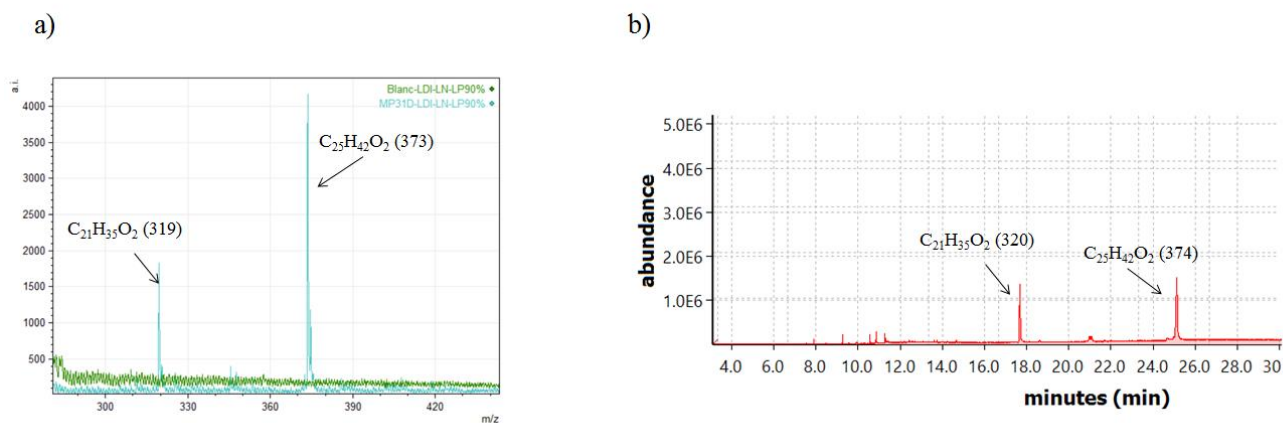




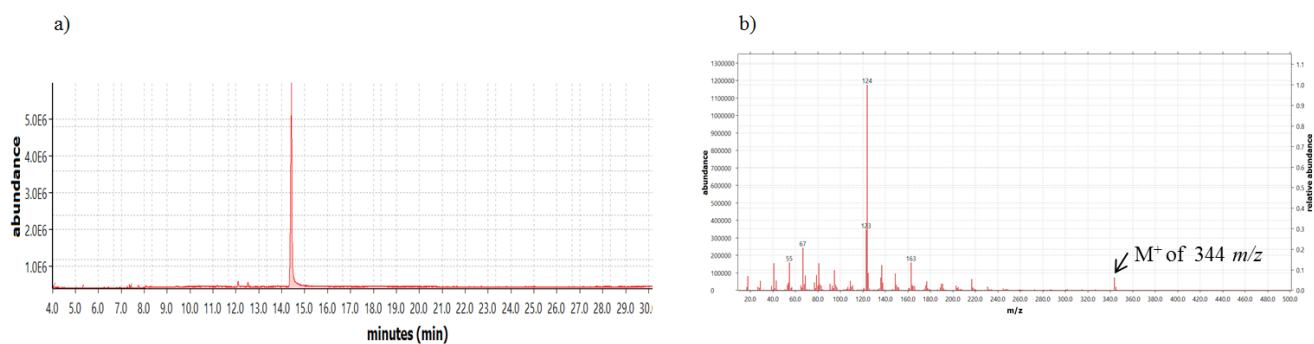
**Figure S10.** Mass spectrum of 1,3-benzenediol-5-(12-heptadecenyl) (3).



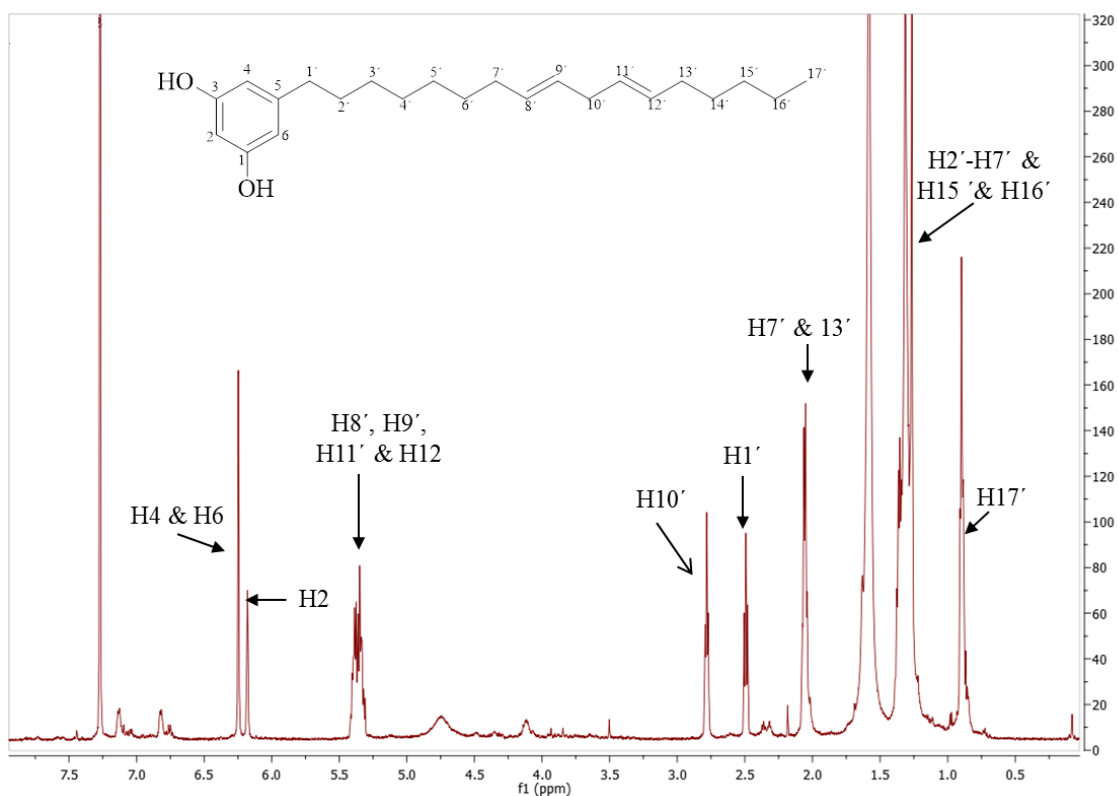
**Figure S11.** Mass spectrum of 1,3-benzenediol-5-(14-nonadecenyl) (4).



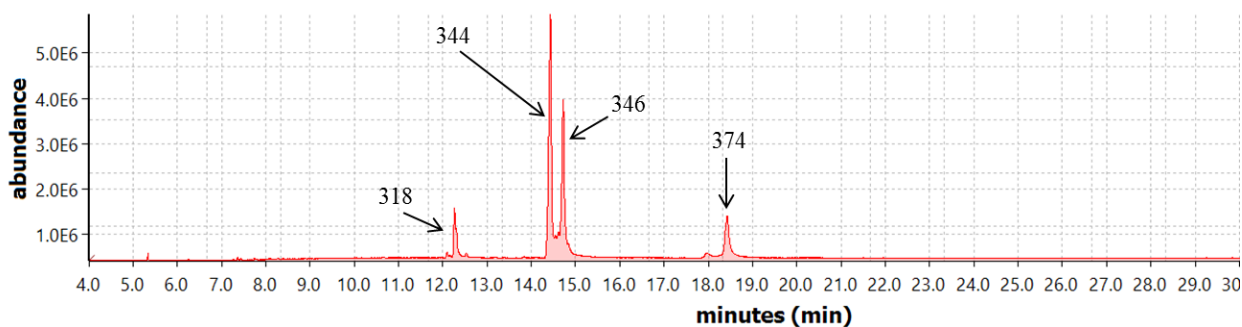
**Figure S12.** (a) LDI spectrum (negative mode) and (b) GC-MS chromatographic profile of purified fraction C4.



**Figure S13.** (a) GC-MS chromatographic profile of purified fraction K4 and (b) fragmentation pattern of the single component with a parent ion peak at  $m/z$  344.



**Figure S14.**  $^1\text{H}$  NMR spectrum (600 MHz,  $\text{CDCl}_3$ ) of purified fraction K4.



**Figure S15.** GC-MS chromatographic profile of purified fraction K3.

## References

1. Funa, N.; Ozawa, H.; Hirata, A.; Horinouchi, S.; *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 6356.
2. Schultz, D. J.; Wickramasinghe, N. S.; Klinge, C. M. In *Integrative Plant Biochemistry - Recent Advances in Phytochemistry*, vol. 40, 1<sup>st</sup> ed.; Romeo, J. T., ed.; Elsevier: Amsterdam, The Netherlands, 2006.
3. Dewick, P. M.; *Medicinal Natural Products*, vol. 1, 3<sup>rd</sup> ed.; John Wiley & Sons Ltd.: Chichester, United Kingdom, 2009.