Supplementary Material

Phytochemical composition of *Denhamia obscura* (A. Rich.) Meisn. Ex Walp. root bark, seeds and leaves

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Experimental

General. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz), using a 5 mm Selective Excitation Inverse (SEI) probe and using solvent peak as internal reference. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and hertz respectively. Merck silica gel (0.043-0.063 mm) was used for flash chromatography. Acetonitrile and ultrapure water were filtered through a microporous glass membrane (0.45 µm) and degassed in an ultrasonic bath prior to use in the HPLC and LCMS systems. Other reagents were directly used as obtained commercially.

A Shimadzu Liquid Chromatography Mass Spectrometer (LCMS) 2020 series coupled with a Photodiode Array (PDA) detector was used in the analysis of crude extracts and fractions. Samples were loaded onto a reverse-phase semi-preparative column (Phenomenex® Luna Omega 5 µm PS C18 100 x 3.0 mm) and eluted with a binary solvent system consisting of Solvent A (formic acid (0.1%)) and Solvent B (95% acetonitrile, 0.1% formic acid). A volume of 10 µL was injected into the system and eluted from the column (40° C) at 0.5 mL/min $^{-1}$ with a mobile phase B held at 5% for 5 minutes followed by linear gradients of B from 5-95% (5-65 min) where it was held until stop at 75 min. The PDA monitored a UV-visible range between 210 and 600 nm, while the MS with Electrospray Ionization (ESI) detected a mass to charge (*m/z*) range between 50-1000 Da in dual mode (positive and negative ions).

A Shimadzu Gas Chromatography Mass Spectrometer (GCMS) QP2010-plus spectrometer was used for sample analysis. Instrument control, acquisition and analysis were conducted using GCSolutions® (Shimadzu, Kyoto, Japan). The analytical column was (Rxi-5SIL-MS column (30 m, 0.25 ID)) eluted at 3.5 mLmin^{-1} (column flow), and a total flow of 97.5 mLmin^{-1}, injection port was kept at 250° C, and the detector 250° C. Temperature of the column was kept at 50° C for one minutes, followed by at 37.5° C min^{-1} increase until reaching 200° C, at which point the temperature is kept constant for 10 min, when it was increased at 20° C min^{-1} until reaching 300° C, where it was held until stop at 30 min. The MS monitored between *m/z* 40-800 with 0.5 sec event time.

Optical rotation was measured with a P-2000 digital polarimeter (JASCO International Co.) data acquisition and procession conducted with Spectra Manager™, path length at 100 mm, aperture at 3 mm, wavelength at 589 nm, integration at 5s, cycle times 20, cycle interval at 10 s, cell temperature at 24° C.

Melting point determined using a Digimelt (SRS) machine (255 - 270° C with 2° C/ min ramp rate).

X-ray Data were collected using an Oxford Gemini Ultra employing confocal mirror monochromated Cu-Kα radiation generated from a sealed tube (1.5418 Å) with ω scans at 190(2) K[1]. Data integration and reduction were undertaken with CrysAlisPro[1] . Subsequent computations were carried out using Olex2.[2] Structures were solved with ShelXT[3] and refined and extended with ShelXL.[4] Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. The Flack[5] parameter unambiguously confirms the absolute structure. $C_{30}H_{50}O$ (*M* =426.70 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 6.3575(2) Å, *b* = 13.9210(5) Å, *c* = 28.4205(11) Å, *V* = 2515.29(15) Å^3, *Z* = 4, *T* = 190 K, μ(Cu Kα) = 0.482 mm^{-1}, *Dcalc* = 1.127 g/cm^3, 11573 reflections measured (7.07° ≤ 2Θ ≤ 122.614°), 3852 unique (R_{int} = 0.0422, R_{sigma} = 0.0363) which were used in all calculations. The final R_1 was 0.0378 (I > 2σ(I)) and wR_2 was 0.0859 (all data). CCDC number: 2150530.

α-D-glucose (**19**): ^{1}H (500 MHz, D_2O) δ_H 5.24 (d, *J*=3.8 Hz, 1H, H-1), 3.83 (d, *J*=12.0 Hz, 1H, H-6a), 3.82 (d, *J*=5.6 Hz, 1H, H-5), 3.76 (d, *J*=12.0 Hz, 1H, H-6b), 3.72 (dd, *J*=10.4, 8.8 Hz, 1H, H-3), 3.54 (dd, *J*=9.5, 5.4 Hz, 1H, H-2), 3.41 (d, *J*=9.5 Hz, 1H, H-4). ^{13}C (125 MHz, D_2O) δ_C 92.7 (1), 73.1 (3), 72.1 (2), 71.9 (5), 70.5 (4), 61.0 (6).NMR data consistent with literature.[6]

β-D-glucose (**20**): ^{1}H (500 MHz, D_2O) δ_H 4.65 (d, *J*=7.9 Hz, 1H, H-1), 3.73 (dd, *J*=12.0, 2.2 Hz, 1H, H-6a), 3.51 (d, *J*=9.2 Hz, 1H, H-3), 3.49 (td, *J*=5.9, 2.2 Hz, 1H, H-5), 3.41 (dq, *J*=9.2, 4.9 Hz, 1H, H-4), 3.48 (d, *J*=12.0 Hz, 1H, H-

6b), 3.25 (dd, *J*=9.2, 7.9 Hz, 1H, H-2). ^{13}C (125 MHz, D_2O) δ_C 96.7 (C1), 77.0 (C5), 76.7 (C3), 74.6 (C2), 70.3 (C4), 61.3 (C6). NMR data consistent with literature.[6]

β-xylose (**21**): ^{1}H (500 MHz, D_2O) δ_H 4.58 (d, *J*=7.9 Hz, H-1), 3.91 (dd, *J*=12.2, 2.2 Hz, 1H, H-5b), 3.63-3.61 (m, 1H, H-4), 3.41 (d, *J*=9.3 Hz, 1H, H-3), 3.34-3.33 (m, 1H, H-5a), (H-2 obscured by glucose H-2 dd at δ_H 3.25). ^{13}C (125 MHz, D_2O) δ_C 96.60 (C1). Compound isolated in low concentration in a mixture with 8 and 9, HSQC signals obscured. NMR data consistent with literature.[7]

Figure S1. ^{1}H NMR spectra for obscurol (**3**) (500 MHz, $CDCl_3$)

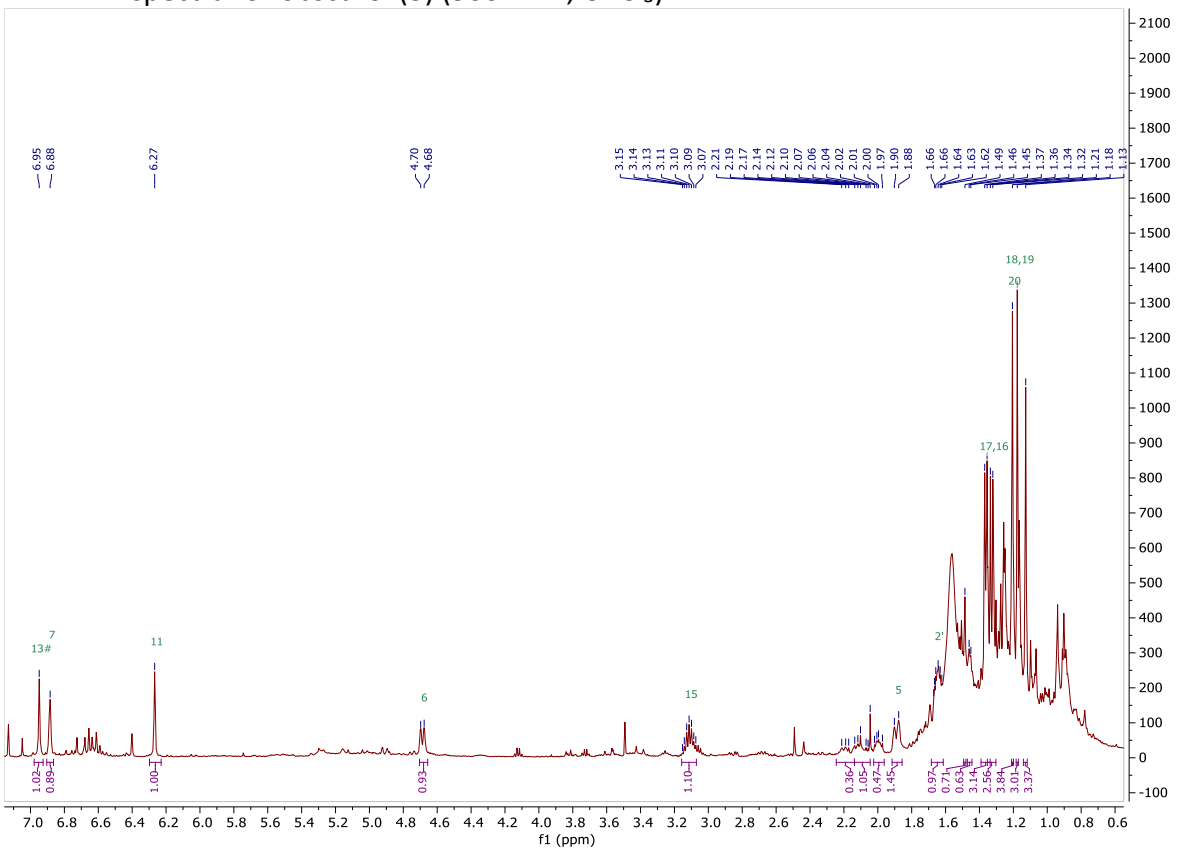


Figure S2. COSY spectra for compound **3** (500 MHz, $CDCl_3$)

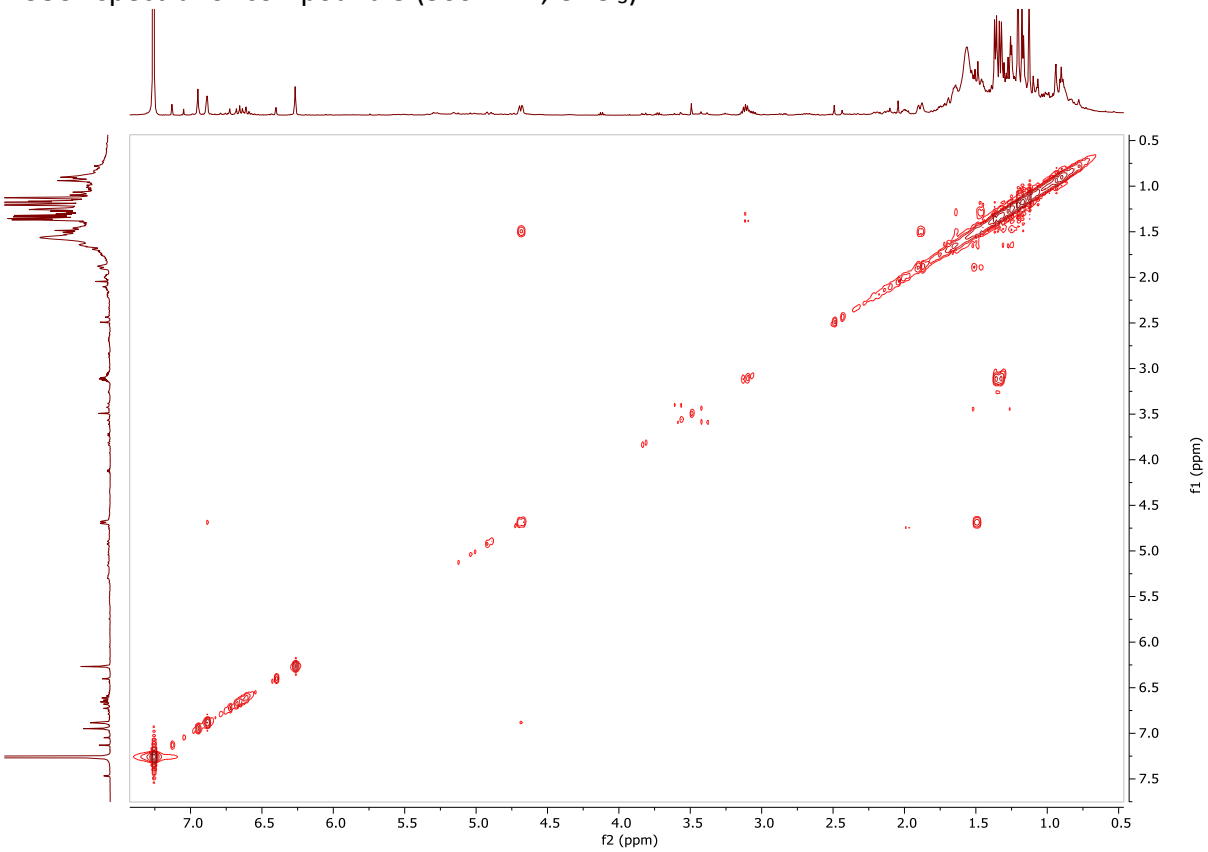


Figure S3. HSQC spectra for compound **3** ($CDCl_3$)

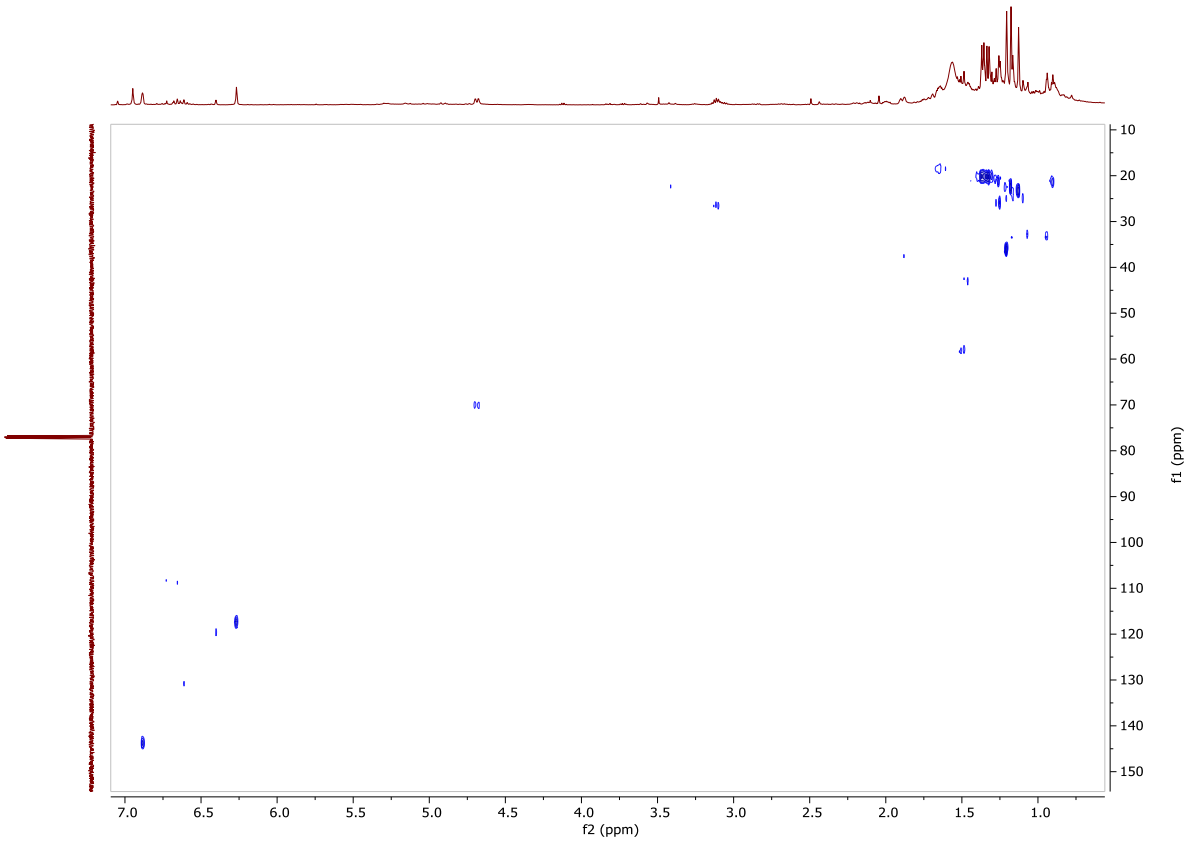


Figure S4. HMBC spectra for compound **3** ($CDCl_3$)

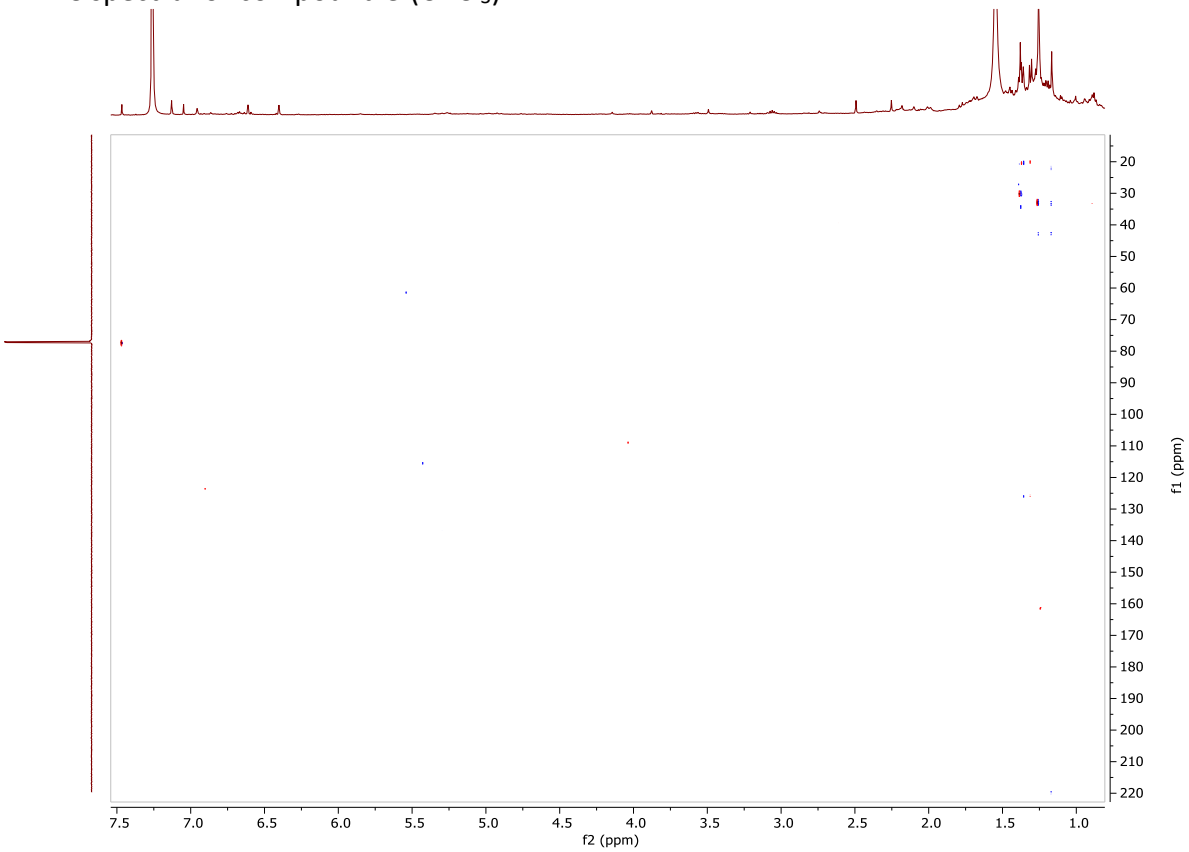


Figure S4.1. HMBC spectra for compound **3** ($CDCl_3$) Zoom

Figure S5. ^{1}H NMR spectra of 13-methoxysempervir-6-ene (**7**) as a minor (~10%) component of a mixture with maytenoquinone (**2**) (500 MHz, $CDCl_3$).

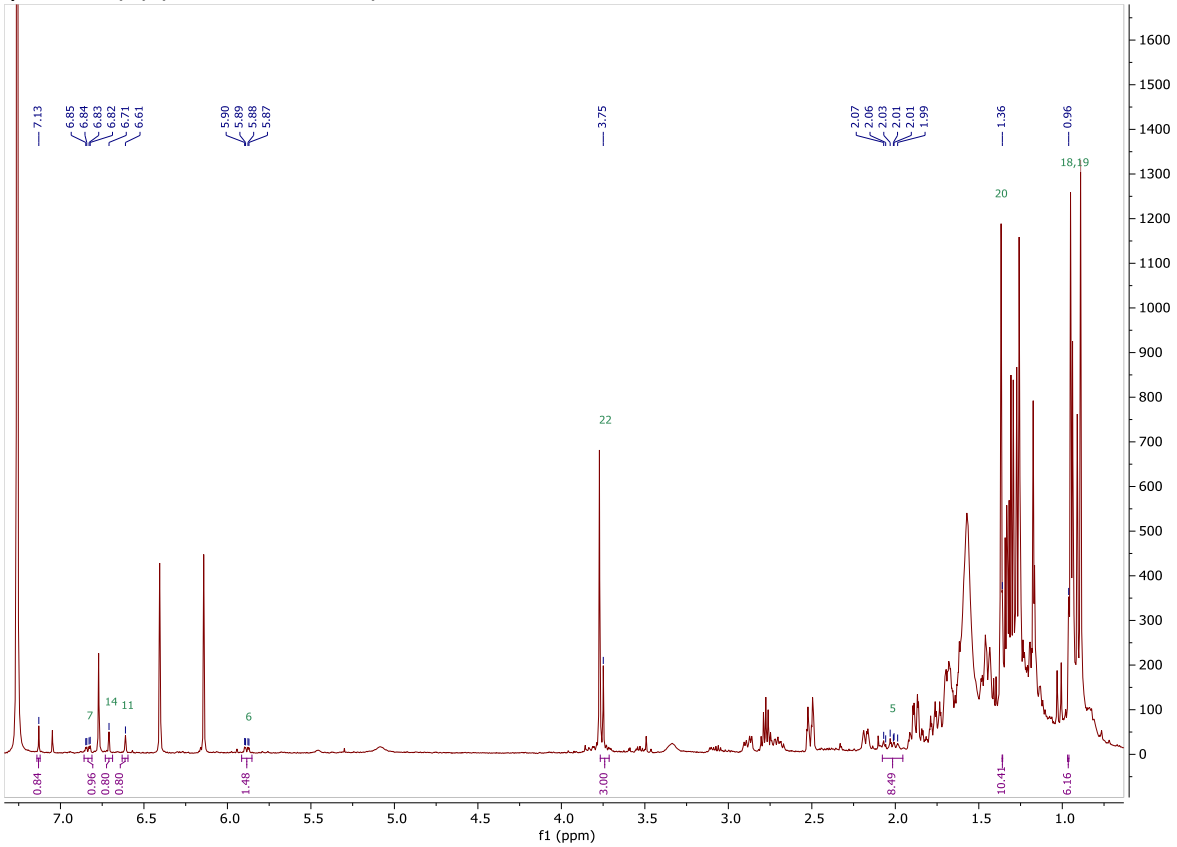


Figure S6. COSY spectra of 13-methoxysempervir-6-ene (**7**) as a minor (~10%) component of a mixture with maytenoquinone (**2**) (500 MHz, $CDCl_3$).

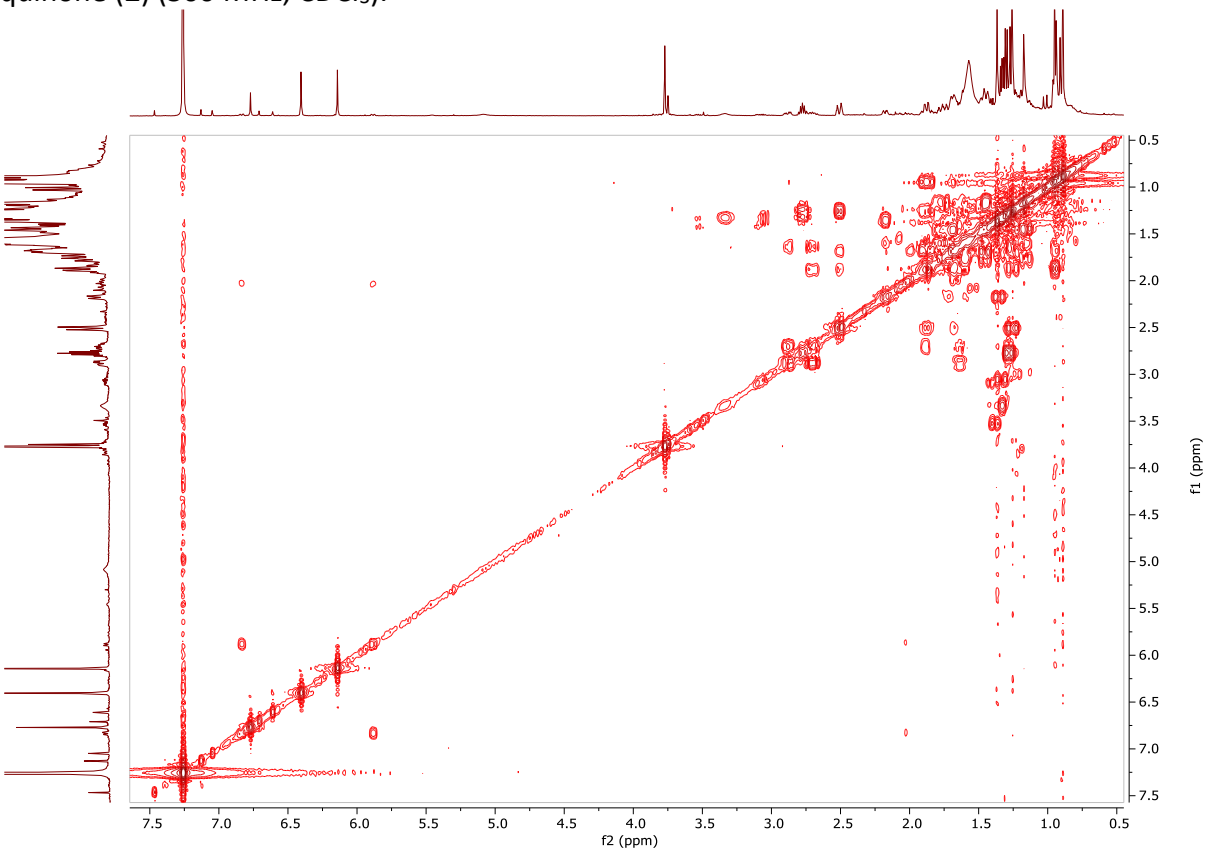


Figure S7. HSQC spectra of 13-methoxysempervir-6-ene (**7**) as a minor (~10%) component of a mixture with maytenoquinone (**2**) (500 MHz, $CDCl_3$).

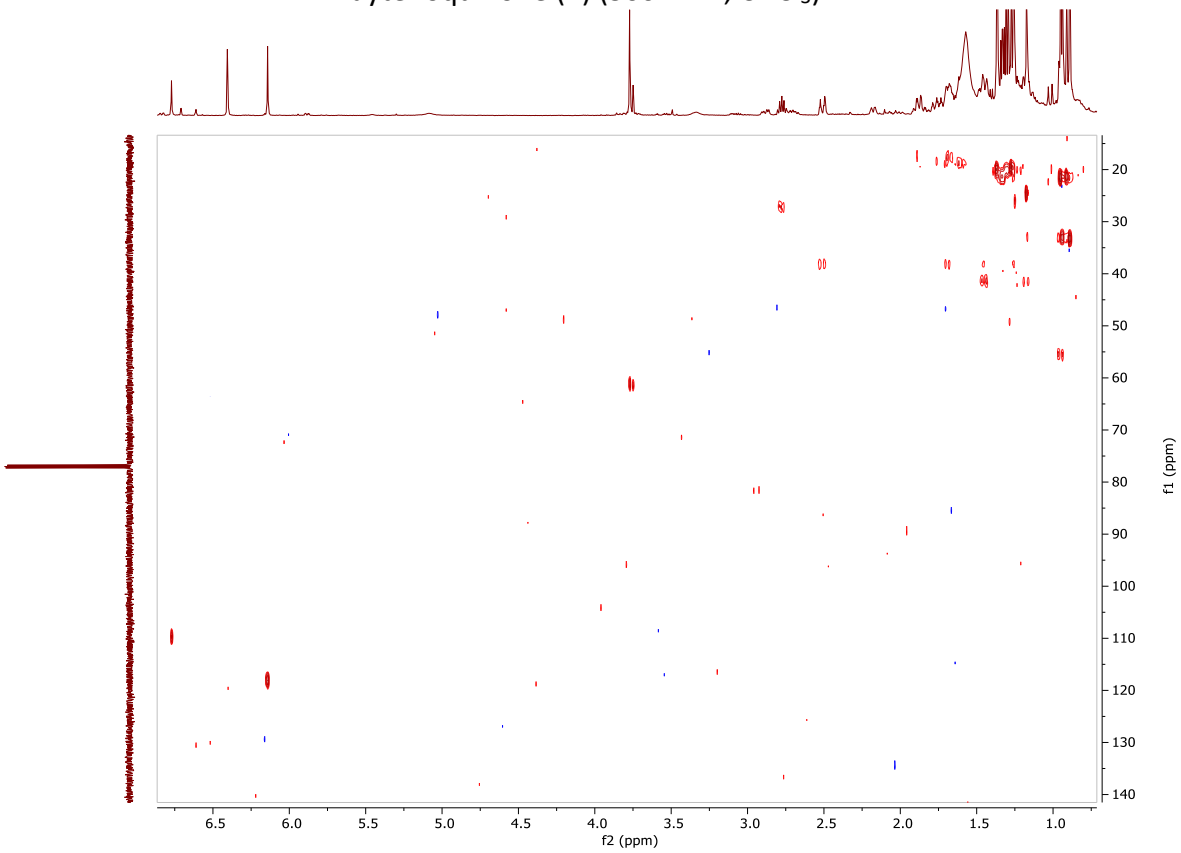
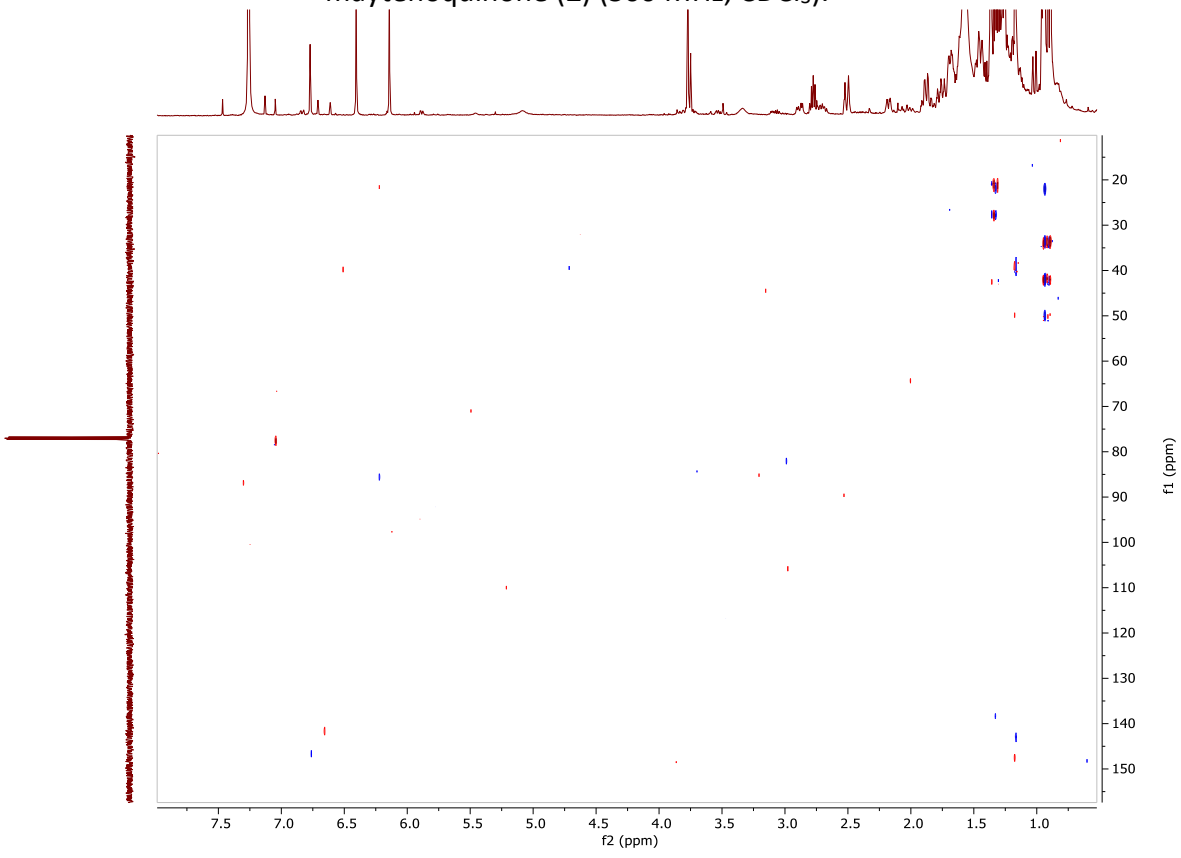


Figure S8. HMBC spectra of 13-methoxysempervir-6-ene (**7**) as a minor (~10%) component of a mixture with maytenoquinone (**2**) (500 MHz, $CDCl_3$).



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