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*Supplement of*

## **The acid-catalyzed hydrolysis of an $\alpha$ -pinene-derived organic nitrate: kinetics, products, reaction mechanisms, and atmospheric impact**

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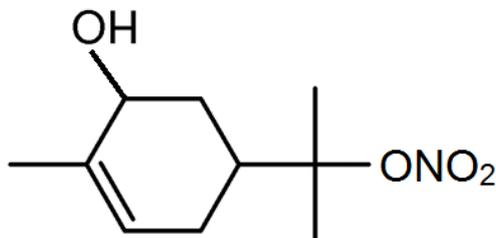
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## S1 Characterization of the $\alpha$ -pinene-derived organic nitrate

### S1.1 NMR data

Here we characterize and verify the structure of the synthetic  $\alpha$ -pinene-derived organic nitrate (APN), shown in Fig. S1, using  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

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**Figure S1: The proposed structure of the synthesized  $\alpha$ -pinene-derived organic nitrate (APN).**

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The chemical shifts (ppm), peak multiplicity and integration of the APN protons in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum (400 MHz), using deuterated chloroform ( $\text{CDCl}_3$ ) as a solvent, were as follows:  $\delta$  1.5 (m, 1H),  $\delta$  1.5 (s, 3H),  $\delta$  1.6 (s, 3H),  $\delta$  1.8 (s, 3H),  $\delta$  1.9 (m, 2H),  $\delta$  2.2 (m, 1H),  $\delta$  2.4 (m, 1H),  $\delta$  4.1 (s, 1H),  $\delta$  5.6 (t, 1H), 20.66, 22.34, 22.46, 26.38, 32.61, 36.07, 68.01, 94.14, 124.27, 134.39.

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The results indicate that the molecule exhibits olefinic character. Most revealing are the downfield shifts in the  $^1\text{H}$  NMR at 5.6 and 4.1 ppm, which are consistent with protons geminal to an olefinic carbon and a hydroxyl group, respectively. No hydroxyl proton were identified in the  $^1\text{H}$  NMR spectrum, likely due to chemical exchange processes. All other protons are accounted for and are consistent with the proposed molecular structure.

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To verify the number and types of carbon atoms in this molecule, the APN was analyzed using  $^{13}\text{C}$  NMR (Bruker ARX400 NMR). The resulting spectra, which includes distortionless enhancement by polarization transfer (DEPT)-135 and DEPT-90 spectra, are presented in Fig. S2.

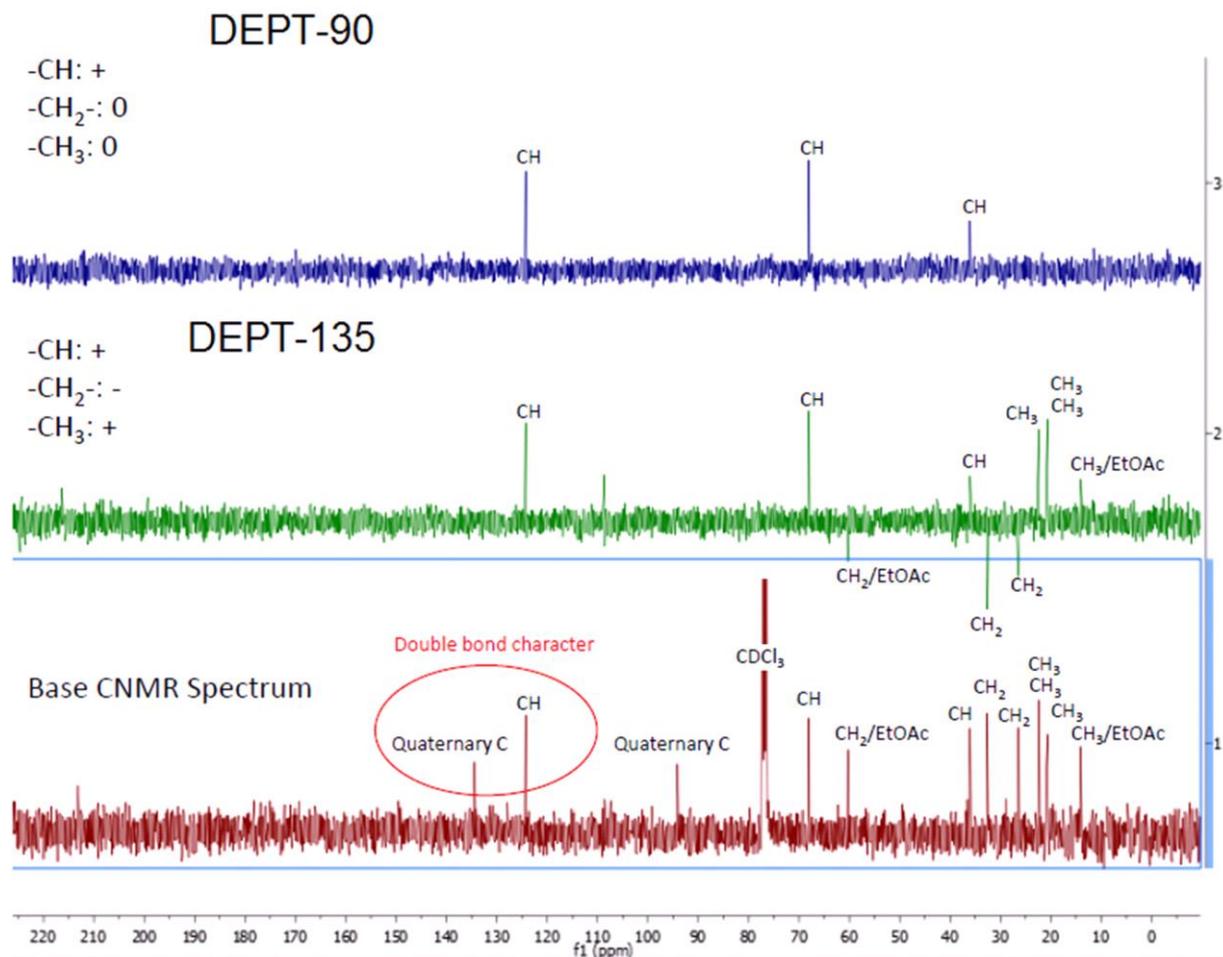


Figure S2:  $^{13}\text{C}$  NMR spectra of the synthesized  $\alpha$ -pinene-derived organic nitrate (APN). The base  $^{13}\text{C}$  NMR spectrum is shown in the bottom panel followed by the DEPT-135 spectrum in the middle panel and finally the DEPT-90 spectrum in the top panel.

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Overall, there are thirteen chemical shifts observed in the base  $^{13}\text{C}$  NMR spectrum, ten that correspond to the synthesized product and three that correspond to ethyl acetate (solvent used during purification). A small signal was observed at  $\sim 110$  ppm in the DEPT-135 spectrum, however, since this signal was not present in the base  $^{13}\text{C}$  NMR spectrum, it is likely a sampling artifact. The results from the DEPT-135, which differentiates  $-\text{CH}_2$  from  $-\text{CH}_3/-\text{CH}$  groups, and the DEPT-90, which identifies  $-\text{CH}$  groups, confirmed the proposed carbon backbone of the synthesized APN.

Most notably, the base  $^{13}\text{C}$  NMR spectrum of the APN is similar to that of *trans*-sobrerol, the analogous diol, with the only exception being a downfield shift of a quaternary carbon from 72.38 ppm to 94.14 ppm, which is consistent with deshielding from a nitrate group (see Fig. S3). Thus, the  $^{13}\text{C}$  NMR results indicate high confidence in the proposed APN structure.

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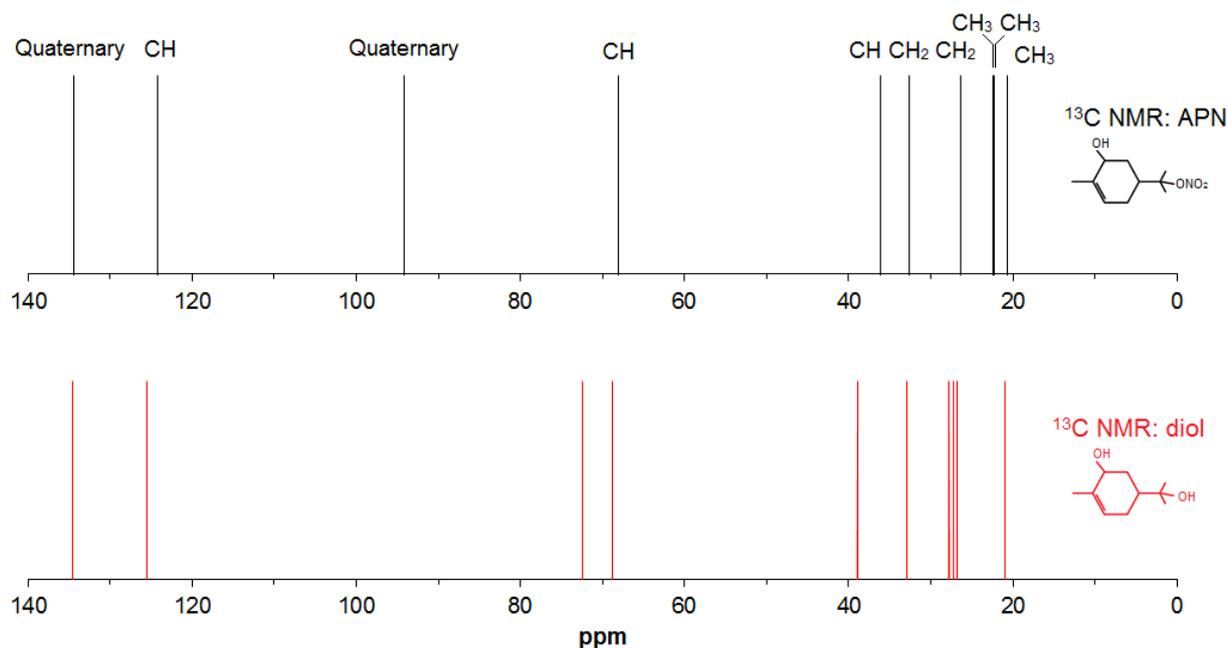


Figure S3: The  $^{13}\text{C}$  NMR data of the synthesized  $\alpha$ -pinene-derived organic nitrate (top) compared to the  $^{13}\text{C}$  NMR data of the analogous diol, *trans*-sobrerol (bottom). The *trans*-sobrerol data provided is from de Silva Rocha et al. (2008).

## 5 S1.2 FTIR data comparison

To verify the nitrate functionality of the synthesized molecule, sample concentration was determined using both  $^1\text{H}$  NMR and Fourier transform infrared (FTIR) spectroscopy. The  $^1\text{H}$  NMR-derived concentration was determined via comparison to a 4-dimethylaminopyridine (DMAP) internal standard of known concentration. The FTIR-derived concentration was determined using the characteristic asymmetric  $-\text{NO}_2$  stretch observed at  $\sim 1640\text{ cm}^{-1}$  for organic nitrates (Nielsen et al., 1995). The instrument was calibrated using an external standard, ethylhexyl nitrate. The  $^1\text{H}$  NMR-derived concentration was calculated to be  $0.31(\pm 0.03)\text{ mM}$  and the FTIR-derived concentration was calculated to be  $0.36(\pm 0.06)\text{ mM}$ . The ratio of FTIR/HNMR calculated concentrations was  $1.16(\pm 0.20)$ , indicating that the two calculated concentrations do not differ statistically and that the product is an organic nitrate.

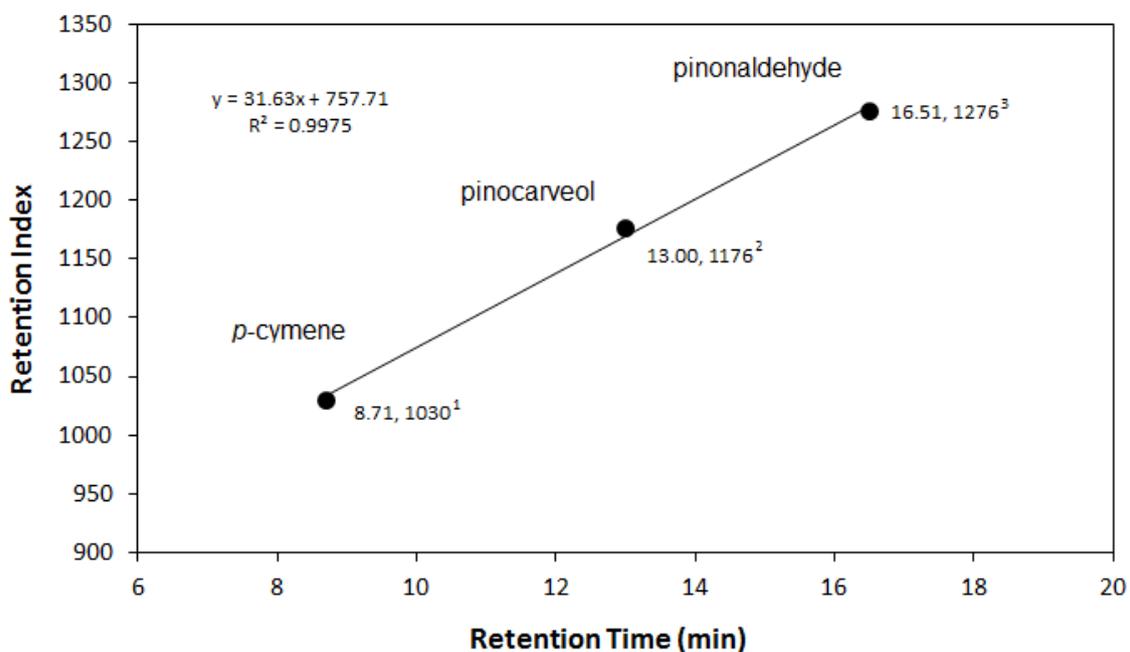
## S1.3 Identification using CIMS

Mass spectrometry was used to confirm the identity of the synthesized APN. The sample was evaporated into a Teflon bag by heating the sample in a stream of purified  $\text{N}_2$  and analyzed using iodine-adduct chemical ionization mass spectrometry (CIMS). The major peak observed in the resulting mass spectrum had a mass-to-charge ratio ( $m/z$ ) of 342, which is characteristic of the  $[\text{M}+\text{I}]^+$  adduct of a monoterpene-derived hydroxyl nitrate ( $M = 215\text{ g mol}^{-1}$ ) (Lee et al., 2016).

## S2 Hydrolysis product characterization

Characterization of the hydrolysis product was accomplished using a QP-2010 GC-MS (Shimadzu, Inc.) equipped with a ZB-1701 column (30 m, 0.25 mm, 1.0  $\mu\text{m}$ ; Phenomenex, Inc.). The column oven was kept at 58°C for 5 minutes before being heated to 255°C at a rate of 8°C/minute.

- 5 Identification of the hydrolysis product pinol was made by comparison to a known EI mass spectrum and retention index (RI). Using the NIST 2014 MS software, a mass spectral comparison yielded a score of 937 out of 999, considered to be an “excellent” match by the software. A linear regression of observed retention times (RTs) and known retention indices of external standards was used to calculate a theoretical RT for pinol, based on a retention index of 1083 (Zenkevich, 1997). See Fig. S4 for the plotted data and information about the standards used. The theoretical RT (10.28 min.) calculated from
- 10 the linear regression was within 3% of the observed RT (10.03 min.), indicating high confidence in the assignment of pinol.



15 Figure S4: Known retention indices of external standards *p*-cymene, pinocarveol, and pinonaldehyde plotted against their observed GC-MS retention times. 1. Jalali-Heravi et al. (2006), 2. Coen et al. (1995), 3. Kallio et al. (2006)

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