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Supplement of

The acid-catalyzed hydrolysis of an α -pinene-derived organic nitrate: kinetics, products, reaction mechanisms, and atmospheric impact

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S1 Characterization of the α -pinene-derived organic nitrate

S1.1 NMR data

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

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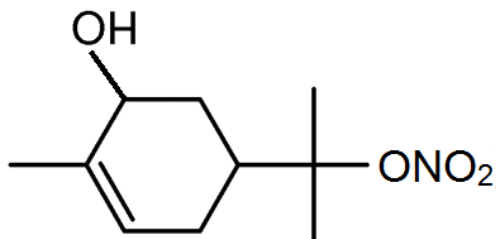


Figure S1: The proposed structure of the synthesized α -pinene-derived organic nitrate (APN).

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The chemical shifts (ppm), peak multiplicity and integration of the APN protons in the ^1H and ^{13}C NMR spectrum (400 MHz), using deuterated chloroform (CDCl_3) as a solvent, were as follows: δ 1.5 (m, 1H), δ 1.5 (s, 3H), δ 1.6 (s, 3H), δ 1.8 (s, 3H), δ 1.9 (m, 2H), δ 2.2 (m, 1H), δ 2.4 (m, 1H), δ 4.1 (s, 1H), δ 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 ^1H 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 ^1H 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}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.

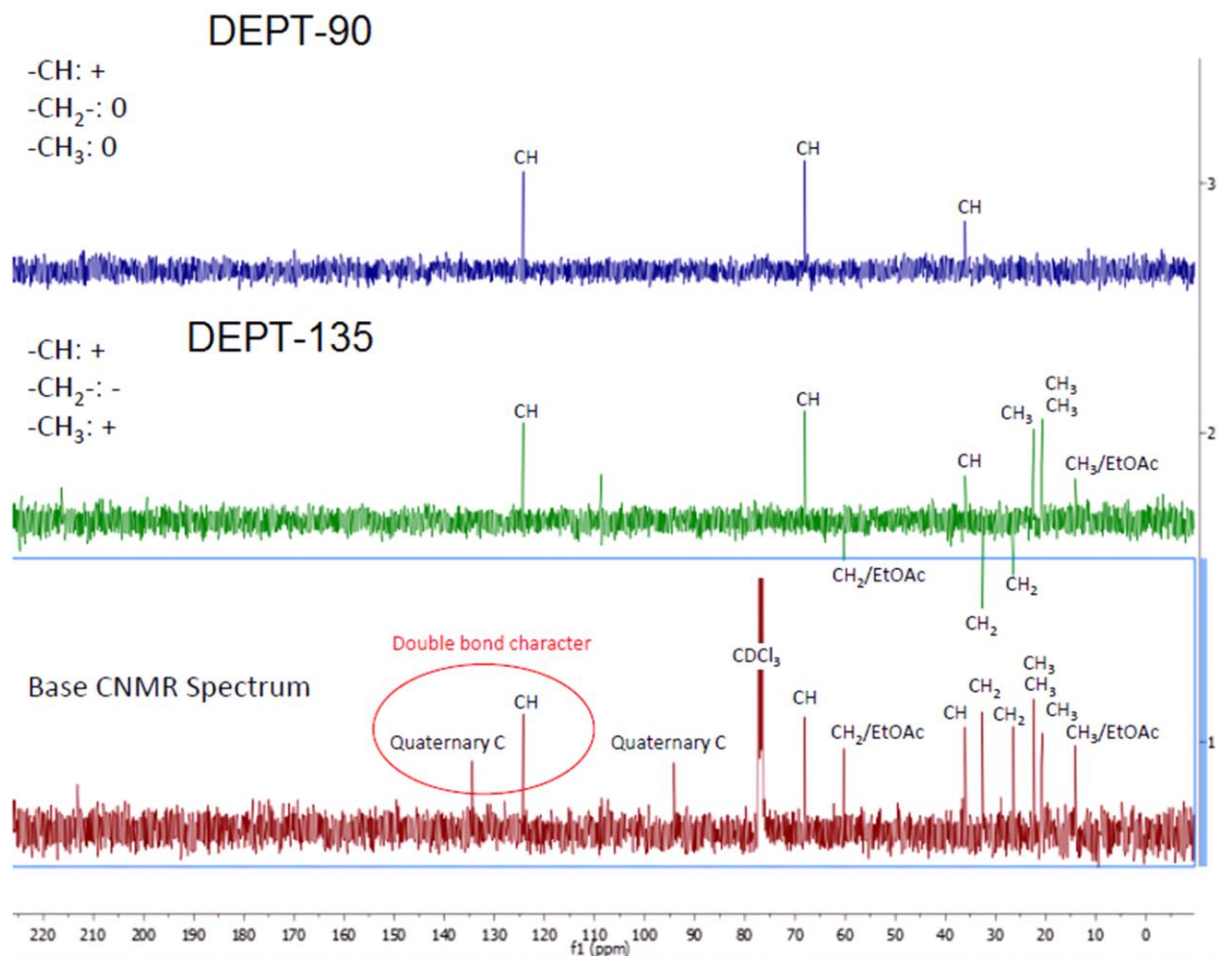


Figure S2: ^{13}C NMR spectra of the synthesized α -pinene-derived organic nitrate (APN). The base ^{13}C NMR spectrum is shown in the bottom panel followed by the DEPT-135 spectrum in the middle panel and finally the DEPT-90 spectrum in the top panel.

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Overall, there are thirteen chemical shifts observed in the base ^{13}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 ~ 110 ppm in the DEPT-135 spectrum, however, since this signal was not present in the base ^{13}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}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}C NMR results indicate high confidence in the proposed APN structure.

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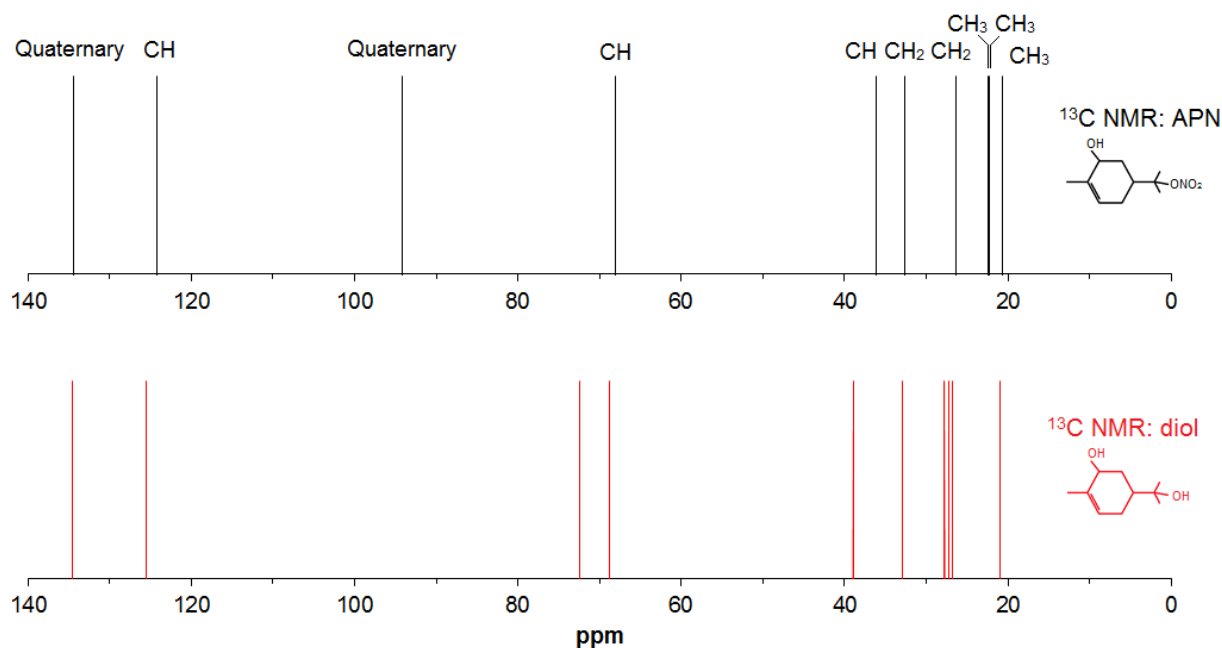


Figure S3: The ^{13}C NMR data of the synthesized α -pinene-derived organic nitrate (top) compared to the ^{13}C NMR data of the analogous diol, *trans*-sobrerol (bottom). The *trans*-sobrerol data provided is from de Silva Rocha et al. (2008).

5 S1.2 FTIR data comparison

To verify the nitrate functionality of the synthesized molecule, sample concentration was determined using both ^1H NMR and Fourier transform infrared (FTIR) spectroscopy. The ^1H 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 ^1H NMR-derived concentration was calculated to be $0.31(\pm 0.03)$ mM and the FTIR-derived concentration was calculated to be $0.36(\pm 0.06)$ 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.

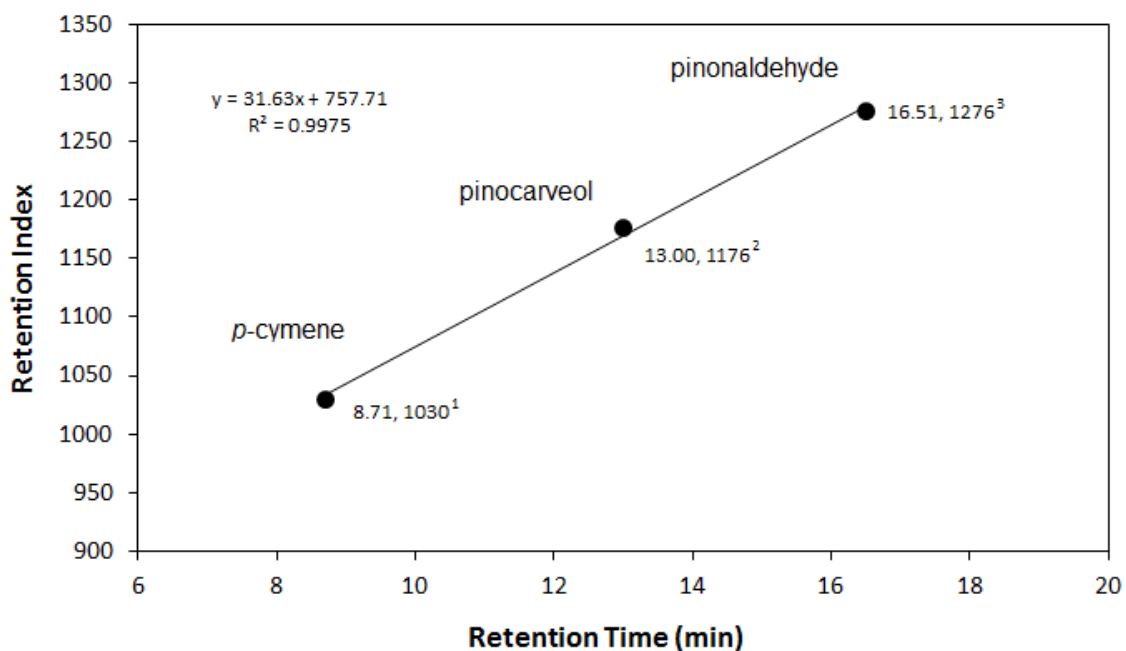
S1.3 Identification using CIMS

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 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 μm ; 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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