

***Interactive comment on “Technical Note:
Preparation and purification of atmospherically
relevant α -hydroxynitrate esters of monoterpenes”
by Elena Ali McKnight et al.***

Anonymous Referee #3

Received and published: 19 August 2019

Note: it appears that superscripts, subscripts, italics and bold type are not recognized by the software. It would be helpful if the editors could provide some means of uploading comments as attachments.

This review is submitted with the benefit of having read reviews of anonymous Reviewers 1 and 2. As stated in the previous reviews, this work contributes procedures for synthesis of a number of vicinal hydroxynitrate esters derived from a monoterpene. The esters can serve as much needed authentic standards for characterizing components of SOA and therefore the work should be published. There are a number of comments that the authors need to address prior to publication.

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Most important: the authors should include ^1H and ^{13}C NMR traces for all compounds that have not been previously reported, and should also include HSQC and HMBC spectra where this is critical for structural elucidation. In particular, the assignment of quaternary carbons is readily evident from the absence of C–H cross peaks in the HSQC spectra.

Since the authors had access to high-resolution mass spectrometry, exact mass measurements and fragmentation patterns should be provided either in the experimental section of the text or the SI for all compounds not previously reported.

Globally, there is considerable carelessness with regard to the presentation of this manuscript. Conventionally, solvent names do not begin with upper case letters and in the case of deuterated solvents, the notation “d” is italicized (e.g., chloroform-[*italicized*]d). This convention is adhered to randomly throughout.

The use of abbreviations for solvents is also not consistent (e.g. EtOAc:Hex and ethyl acetate:hexanes (solvent and compound names are inappropriately capitalized in the text)).

Several citations are only partially given in the text (e.g. Cocker, 1969 on p. 4, l. 8) and in one case, a citation in the text is missing from the bibliography (Charbonneau, 2018; Charbonneau was misspelled).

There are mistakes in nomenclature: trans-3-carene (not trans-(3)-carene). Synthetic targets are referred to as “title” compounds. However, “target compound” would be preferable, since compounds do not appear in titles.

Reaction/synthetic schemes should be separated from tables and figures and appropriately designated. Although the comments above are editorial and easy to correct, the resulting impression is a lack of care in preparation of the manuscript.

There are also some specific issues that need to be addressed: 1. The authors might note that products having two or more asymmetric carbons were isolated and charac-

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terized as mixtures of diastereomers. Visual inspection of the NMR spectra does not appear to show any resolution of the mixture by NMR. Did the authors look for any such result?

2. For the preparation of trans-carene oxide (p. 3, starting with l. 17), did the authors start with optically pure (+)-carene or a racemic mixture? This is important, since epoxidation with mCPBA will give an enantiomerically pure epoxide from enantiomerically pure starting material. The synthesis of the cis oxide described below apparently starts with (+)-carene.

3. Preferred nomenclature for cpd 20 would be 2-methyl-5-(propan-2-ylidene)cyclohex-2-en-1-ol.

4. Visual inspection of the ¹H NMR trace of cpd 24 appears to be consistent with the signal at 5.31 ppm as a poorly resolved doublet-of-doublets. It is not clear how the authors interpreted this signal as a doublet-of-doublets-of-doublets.

5. p. 7, l. 16 and following; p. 13, l. 3 and following: As pointed out by Reviewer 1, there is a problem with the structural assignment of limonene 8,9-dihydrodiol (10) to the crude product of Bi(NO₃)₃ treatment of limonene 8,9-oxide (9). This is true as well for the rearrangement product 2-(4-methylcyclohex-3-en-1-yl)propanal (preferred nomenclature) (11). The ¹H NMR data provided do not match published data for either proposed structure (diol: J. Am. Chem. Soc. 2018, 140, 1502–1507; aldehyde: Phytochemistry 2017, 144, 208 – 215). This reviewer notes that the reported ¹H NMR of the diol was acquired at a spectrometer frequency of 600 MHz, although the only expected difference would be improved resolution of the proton splittings.

6. On p. 11, starting with line 12: The authors should provide additional discussion justifying the structural assignments of cpds 27 and 29. Neither of these compounds appears to have been structurally characterized by NMR in the literature. In the ¹H NMR spectrum of 27, the signal at ~5.6 ppm appears to be a broad doublet. It is unclear why the authors have used the designation “multiplet”. In the ¹H NMR spectrum of 29,

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which is a racemic mixture, the lowest field signal (H attached to the nitrate-substituted C) should be a singlet, as it appears to be. Why is it described as a doublet?

7. Figure 2: The authors should add the diol and aldehyde structures to this scheme. There is sufficient space and this gives the true picture of reaction products.

8. p. 12, l. 15: The phrase, “. . .assigned to the methyne adjacent to the alcohol...” should be rewritten as “. . .assigned to the alcohol methyne carbon...” As written, the statement “adjacent to” is confusing. Where heteronuclear correlations are important in verifying structure, the 2D spectra should be added to the SI. As pointed out above, it would be helpful if all the NMR data were included in SI.

9. p. 12, l. 17: The rationale for assigning the quaternary carbon would be better explained by stating that no C–H cross peak was observed for the ¹³C signal at 95.6 ppm in the HSQC experiment.

10. p. 16, l. 12: “Epimer” is misused here. Platydiol (the name “platydiol” automatically designates the the di-endo geometry of the diol) has a plane of symmetry, and there are no optical isomers.

11. p.17, l. 14: In discussing the structural verification of nitrate ester 27, it would be helpful to include the HSQC spectrum. As presented in the text, there is not enough data to be convincing regarding the structural assignment.

12. p. 17, bottom: The table of spectral data should have the heading at the top.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2019-690/acp-2019-690-RC3-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-690>, 2019.

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