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Interactive comment on “Terpenylic acid and related compounds: precursors for dimers in secondary organic aerosol from the ozonolysis of α - and β -pinene” by F. Yasmeen et al.

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We thank anonymous reviewer #1 for constructive comments which helped to improve our manuscript. Our responses to the specific comments raised by the reviewer are as follows:

Page 10867 lines 4-7 The sentence is a bit unclear and the statement is not fully qualified by the data. How does mass spectrometric evidence for deprotonated molecules lead to the conclusion that diaterpenylic acid is a key monomeric unit?

Re: The sentence has been modified as follows: “Based on mass spectrometric evidence for deprotonated molecules formed by electrospray ionization in the negative

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ion mode and chemical considerations, it is suggested that diaterpenylic acid is a key monomeric intermediate for dimers of the ester type." The detailed information and discussion will be provided in the main text.

Introduction: The first paragraph should be rewritten to give a broader introduction to the general reader (including a few references).

Re: A broader introduction will be provided for the general reader in an additional introductory paragraph: "The formation of higher-molecular weight (MW) products is considered as a driving force for secondary organic aerosol (SOA) formation and growth, because their formation leads to products with a substantially decreased vapor pressure that is several orders of magnitude lower than the precursor hydrocarbons. Higher-MW products either correspond to non-covalent dimers between monomeric carboxylic acids that are held together by hydrogen bonds (e.g., Hoffmann et al., 1998; Claeys et al., 2009) or to covalent dimers between monomeric carboxylic acids that are linked together through covalent bonds such as esters (e.g., Hamilton et al., 2006; Szmigielski et al., 2007; Müller et al., 2008), and oligomers formed through gem-diol intermediates (e.g., Gao et al., 2004; Iinuma et al., 2004; Tolocka et al., 2004; Docherty et al., 2005) or aldol condensation reactions (e.g., Tolocka et al., 2004). Heterogeneous processes such as these are consistent with the observation that sulfuric acid seed aerosol catalyzes the formation of SOA (e.g., Jang et al., 2002; 2003; Czoschke et al., 2003; Iinuma et al., 2004)." Additional references: - Jang, M. S., Czoschke, N. M., Lee, S., and Kamens, R. M.: Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions, *Science*, 298, 814–817, 2002. - Jang, M., Lee, S., and Kamens, R. M.: Organic aerosol growth by acid-catalyzed heterogeneous reactions of octanal in a flow reactor, *Atmos. Environ.*, 37, 2125–2138, 2003. - Czoschke, N. M., Jang, M., and Kamens, R. M.: Effect of acidic seed on biogenic secondary organic aerosol growth, *Atmos. Environ.*, 37, 4287-4299, 2003.

p. 10869 L 14-16: The words about "major" and "minor" products should be rephrased since I assume that the authors refer to compounds with major/minor intensity in the

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Re: The products do refer to compounds with a high/low signal intensity in the LC/MS chromatograms; correction will be made: "In the present study, we address the structure of a relatively abundant MW 358 compound and related weak MW 344 and 358 compounds . . ."

Experimental: Details of filter sampling at IfT are missing (e.g. air volume and filter type).

Re: The requested details will be provided: "Aerosol samples were collected on a 47 mm PTFE filter (Pall, Fiberfilm) and a volume of 2 m³ was sampled."

10871 L 15-17: This paragraph seems to be out of context.

Re: This paragraph will be removed.

10872 L7: What is an isobaric compound?

Re: An isobaric compound is a compound with the same elemental composition (thus with the same m/z value for their deprotonated molecules) but a different structure, i.e., a compound with a different positional isomeric structure or a non-isomeric compound containing different functional groups. This information will be provided where the term "isobaric" is used.

10872 L21: This is unclear and not precise.

Re: The sentence has been rephrased as follows: "In this section we deal with the structural characterization of terpenoic acids that serve as monomeric precursors to the dimeric MW 344 and 358 compounds that will be addressed in the next sections as well as with the structural characterization of some minor monomeric/isobaric compounds."

10872 L27-> The structure and interpretation of MS spectrum of homoterpenylic acid should be in the paper, not supporting material, since this compound, to my knowledge, has not been studied previously in aerosols.

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Re: The structure and interpretation of the MS data of homoterpenylic acid will be moved to the main text.

10874 L17: The mass of $[M-2H + Na]$ must be m/z 379, which is actually not seen in the mass spectrum. Please clarify.

Re: The m/z value of $[M-2H + Na]^-$ is indeed 379; the ion at m/z 377 could not be assigned. The sentence will be modified as follows: “The first-order mass spectrum (Fig. 4a) shows in addition to the deprotonated molecule $[M-H]^-$ (m/z 357), an ion at m/z 377 which was not assigned, and an ion at m/z 343 due to co-elution of a homologous MW 344 species (see below).”

10874 L21-23: This sentence is unclear and the statements should be discussed a bit more thoroughly.

Re: We write here: “However, there are differences in the relative abundances of the product ions, a feature which can be explained by a different internal energy of the first- (MS2) and second-generation (MS3) precursor ions.” We believe this sentence is formulated correctly from a mass spectrometric point of view. A sentence has been added to provide some additional explanation: “Precursor ions with a higher internal energy will namely result in more extensive fragmentation upon MS2 or MS3 collisional activation experiments.”

10876: The statements on unique dimer-forming properties of both terpenylic and terebic acid are too strong. How do we know that there are not other, maybe yet unidentified, compounds with this property? But it seems that terpenylic acid forms dimers more readily than norpinic acid. Structures of terebic and diaterebic acid as well as interpretation of mass spectra should be in the paper, not supporting material.

Re: The adjective “unique” has been replaced by “strong”; it is indeed possible that there are other yet unidentified compounds with this property. The structures of terebic and diaterebic acid acetate and the discussion of their mass spectra will be moved to

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the main text.

10877 L10-20: This paragraph is difficult to read due to long and unclear sentences.

Re: An effort will be done to improve the readability of this paragraph by using shorter sentences: "We also evaluated whether the higher-MW 368 product, which was reported by Müller et al. (2008) and corresponds to a diester formed between cis-pinic acid and 10-hydroxypinonic acid, was present in our samples. We also compared its abundance with that of the relatively abundant MW 358 compound. The MW 368 compound could be detected at RT 25.9 min for α - and β -pinene ozonolysis SOA, and the ambient samples, with an abundance of about 54%, 1.5%, and 54% of that of the MW 358 compound, respectively. Furthermore, we also evaluated whether higher-MW dimers (MW 372) containing cis-pinic acid and the hydrolysis product of homoterpenylic acid (i.e., diahomoterpenylic acid) could be detected in β -pinene ozonolysis SOA and the ambient samples considering that homoterpenylic acid is present in these samples, but no evidence could be found for them."

10877 L26: "lends support" please change to for example "is in line with previous results" or "supports previous findings".

Re: The correction will be made.

10878 L8-11. This sentence is unclear - both the words and the physical meaning of the sentence.

We have modified the sentence as follows: "This behavior contrasts with the fast formation of the MW 358 diester in alpha- and beta-pinene ozonolysis experiments, which is formed concurrently with the corresponding monomeric precursors."

Figure 1. There is too little information in the figure text.

Re: More details will be provided in the legend to the figure.

Figure 3. Were these MS spectra obtained with standards? What are the retention

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times?

Re: These mass spectra were obtained with authentic standards. This will be mentioned in the legend of the Figure, as well as their retention times.

Scheme 1: Proposed MS-fragmentation, I assume?

Re: The correction will be made.

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