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## ***Interactive comment on “Formation and occurrence of dimer esters of pinene oxidation products in atmospheric aerosols” by K. Kristensen et al.***

### **Anonymous Referee #2**

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This manuscript reports the investigation of dimer esters formed by oxidation of pinene. The results of various chamber studies and two field campaigns (BEARPEX 2007 and 2009) are presented. The focus of these studies is the pinyl-diaterpenyl (MW 358) and the pinonyl-pinyl dimer ester (MW 368). Both compounds seem to be formed very rapidly within 30 min in chamber experiments. However, as a consequence of the low time resolution of the analytical methodology no specific evidence was delivered. Likewise, no conclusive evidences for the formation pathway (particle vs. gas phase formation mechanism) were reported. The field studies took place in the Sierra Nevada Mountains in September 2007 and July 2009. While the pinyl diaterpenyl ester was found in both campaigns, the pinonyl pinyl ester was only found in the 2009 cam-

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paign. A much higher concentration of the first one was found but also a relatively good correlation between them, therefore a similar formation pathway could be suggested. The pinyol diaterpenyl ester concentration could not be correlated to the pinyol and terpenyl acid (TA) concentration, which are possible precursors. But some correlation between the ester and diaterpenylic acid acetate (DTAA) was observed for the 2009 campaign. It was observed that higher temperatures increase the concentration of the esters (field and chamber studies) and also nighttime concentrations are observed to be higher than daytime concentrations. The publication is recommended after some revisions.

Remarks and revisions:

1. The method how the authors quantify especially the esters is highly uncertain. The authors neither use calibration standards nor a chemically similar substance, they just use their precursors – a method that can lead to large errors. Certainly it would be nice to have absolute concentration values for the esters, however, it is certainly better to make only a relative quantification. Actually, for the main conclusions of the manuscript, the absolute concentrations are not necessary and relative values are appropriate.
2. The higher tendency of artifact dimers to form sodium adducts can also result from a higher sodium concentration in this kind of sample than in “normal” air samples.
3. It is reported that pinyol diaterpenyl ester shows a better correlation with DTA and DTAA than with TA. Although the formation of the latter two compounds is different (Claeys et al. (2009)), there is probably a mainly pH-dependent relation between DTA and TA. Also the reaction of DTAA to DTA or terpenylic could be a simple also pH-dependent reaction. Can a better correlation be found with all three compounds combined?
4. In section 3.2.3. it is mentioned for the first time that the  $\alpha$ -pinene concentration is much higher in 2009 than in 2007. This should be done earlier and mentioned during the discussion of the different quantities of the oxidation products.

5. Especially Figure 6 would be easier to comprehend if the values were normalized.

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