Secondary Organic Aerosol Formation and Particulate Products from the Atmospheric Oxidation of 1,8-Cineole

Olaf Böge (1), Yoshiteru Iinuma (1), Melita Keywood (2) and Hartmut Herrmann(1)

(1) Leibniz-Institut für Troposphärenforschung Leipzig,
(2) CSIRO Marine and Atmospheric Research, PMB 1, Aspendale, Australia

Introduction

It is well recognized that the atmospheric oxidation of monoterpenes leads to secondary organic aerosol (SOA) formation through condensation of low volatile oxidation products on preexisting particles. It is estimated that biogenic SOA contributes significantly to the total global particulate carbon load, ranging from 12 to 70 Tg SOA y^{-1} (1).

The eucalypt group contains genera *Eucalyptus*, *Corymbia* and *Angophora* and nearly 900 species and subspecies are recognized mainly in Australia (2). They are the most dominant tree species in the Australian forests and a variety of eucalypt species are used in plantation forests worldwide, especially in tropical, subtropical and temperate regions for productive and protective purposes (2,3). It is reported that some of commonly cultivated *Eucalyptus* species are high monoterpene emitters (4). For these species 1,8-cineole (eucalyptol) is typically the most predominant compound emitted followed by α-pinene, β-pinene or limonene depending on the species (4).

1,8-Cineole mainly reacts with OH-radicals in the troposphere through H-abstraction mechanisms. The estimated tropospheric lifetime of cineole is one day, which is substantially longer than other biogenic organic compounds (5). Even with this lifetime, 1,8-cineole is likely to play an important role in tropospheric photochemistry in regions where high 1,8-cineole emitter species are dominant. Therefore, the OH-radical initiated oxidation of 1,8-cineole was studied in an aerosol chamber with special focus on the resulting particulate products. The results are compared to products found in field measurements.

Experimental

Aerosol Chamber Experiments: The aerosol chamber experiments were performed in the IfT indoor chamber LEAK. The chamber has a Volume of 19 m^3. The chamber is equipped with analyzers for ozone, NO and NO_2, sensors for temperature and humidity. The mixing ratio of 1,8-cineole was monitored using a PTR-MS. Seed particles were produced by nebulyzing a solution 0.06M Na_2SO_4 solution (neutral seed) and acidic seed particles were generated from a 0.03M/0.05M $(NH_4)_2SO_4/H_2SO_4$ mixture solution. Particle size distributions were monitored every 5 minutes using a differential mobility particle sizer (DMPS) system. Two sets of experiments were performed for 1,8-cineole SOA formation. For low NO_x experiments, ozonolysis of of tetramethylethylene (TME) was used as dark source of OH-radicals. In the experiments performed in presence of NO_x the OH-radicals has been produced photolytically.

Field Samples: The ambient samples were collected at the CSIRO Marine and Atmospheric Research (CMAR) Bayside Air Quality Station at Aspendale in Melbourne, Australia (38°01'S and 145°03'E). The side is influenced by vehicle emissions, marine aerosol, light industry and residual emissions. The samples collected on 22, 25 and 28 January 2006 were used for analysis. The period is characterized by hot and humid weather with a number of bushfires in surrounding forests.

Analytical Method and Sample Preparation: The Teflon filters (chamber experimets) or quartz fibre filters (field samples) were extracted in methanol, dried under a gentle stream of N_2 and reconstituted in a methanol/water solution (50/50) for analysis. An HPLC System (1100 series, Agilent) simultaneously coupled to ESI-TOFMS and ESI-ITMS^n (microOTOF and Esquire 3000plus, Bruker Daltonics) were used to characterize the detailed chemical structures of 1,8-cineole oxidation products. Additionally diaterpenylic acid acetate (3-[1-(acetyloxy)-1-methylethyl]glutaric acid) was synthesized as reference.
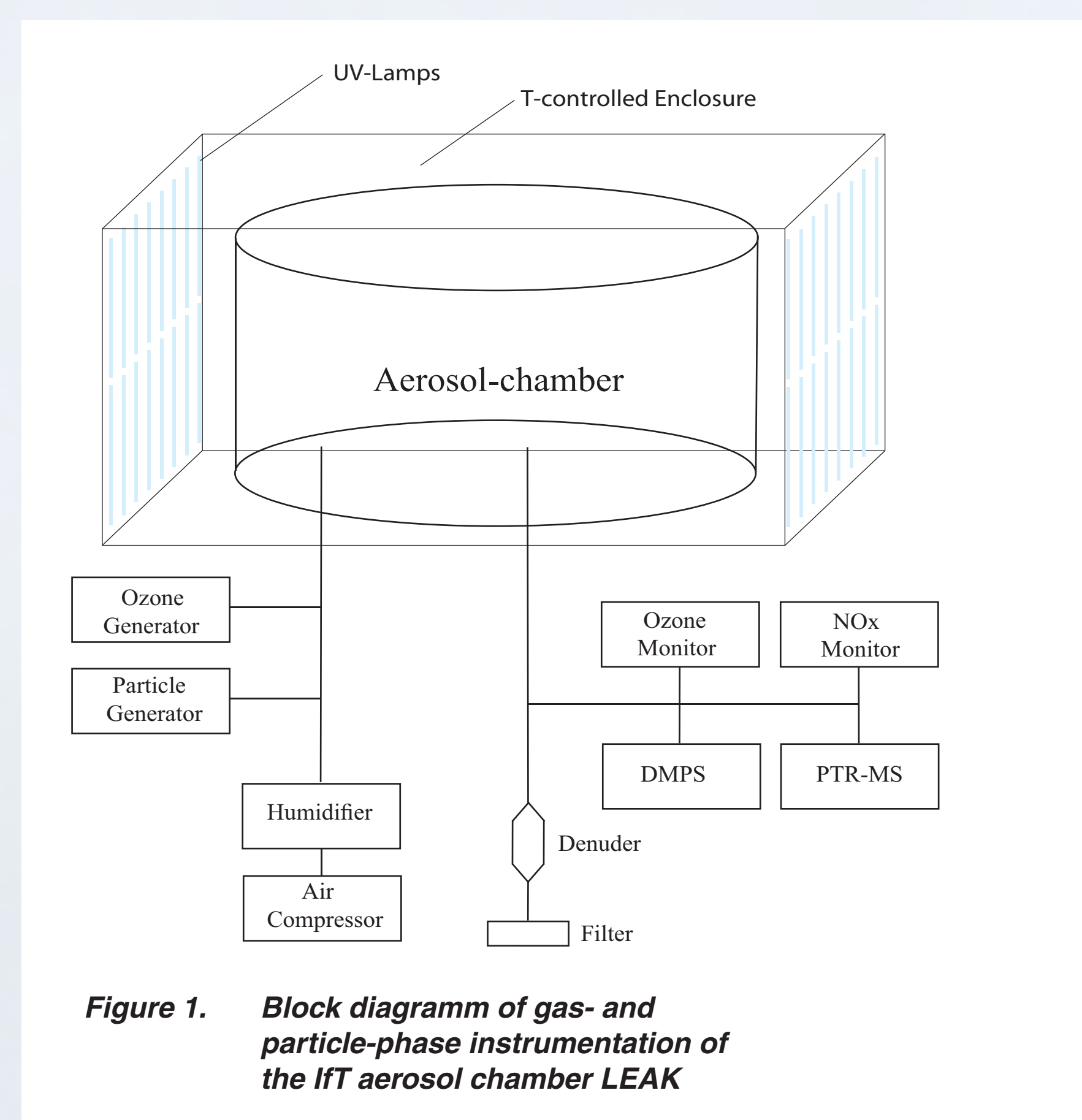

Figure 1. Block diagramm of gas- and particle-phase instrumentation of the IfT aerosol chamber LEAK

Results

SOA Yields: Figure 2 shows SOA yields (Y) as a function of the mass concentration of formed SOA (ΔM_0). Interestingly, the SOA yield in the high NO_x experiment increases sharply until $\Delta M_0 \sim 5$ µg m^{-3}, then it reaches a plateau. The SOA yield data for the low NO_x experiments show a much stronger ΔM_0 dependency throughout the range. This indicates that compounds with extremely low volatility are produced rapidly in the initial phase of the high NO_x experiment, whereas this compounds are formed gradually throughout the course of the low NO_x experiments. Overall, the final SOA yields are somewhat lower for the high NO_x experiment, consistent with other monoterpenes.

Identification of Diaterebic Acid Acetate and Diaterpenylic Acid Acetate: Figure 3 shows base peak chromatograms from the analysis of an ambient sample taken at Melbourne, 1.8-cineole oxidation experiments and a reference compound for peak 9. Major peaks detected in the ambient sample are malic acid (1), succinic acid (2), unknown monoterpene oxidation products (peaks 3, 4, 5, 8 and 9), 3-methyl-1,2,3-butanetricarboxylic acid (6) and phthalic acid (7). For the peaks 8 and 9, chemical formulae of $C_9H_{13}O_6^-$ (m/z 217) and $C_{10}H_{15}O_6^-$ (m/z 231) are determind from TOFMS data, respectively. No comparable peaks were found in our previous terpene ozonolysis studies and no equivalent chemical formulae were reported in the literature. These two peaks are further characterized using ITMS^n cf. Figure 4. The spectra of both compounds show neutral losses of 44u (CO_2) and 60u (actate ester group). The results from the analysis of the chamber samples show that both compounds are present in the chamber samples as two of the most abundant peaks (Figure 3) and their TOFMS and MS^n agreed well with the ambient ones (Figure 4). Based on the interpretation of the mass spectra, a reference compound (Diaterpenylic acid acetate) was synthesized. Its chromatographic (Figure 3) and mass spectral behaviour agree extremely well. The results show that emissions from eucalyptus trees contributes significantly to the SOA loading in the region and it may play an important role in the regional air quality.
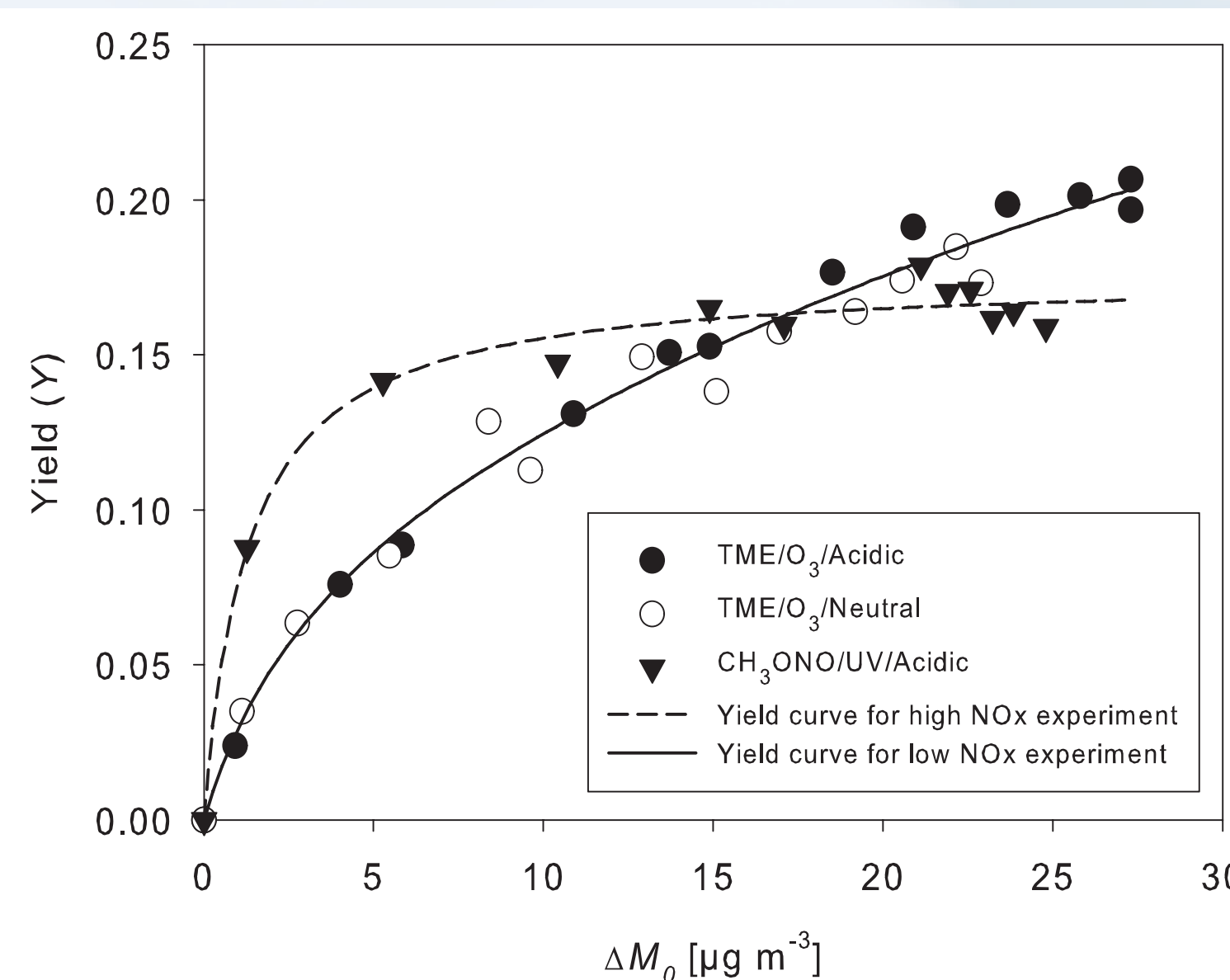

Figure 2. SOA yields as a function of the mass concentration of formed SOA
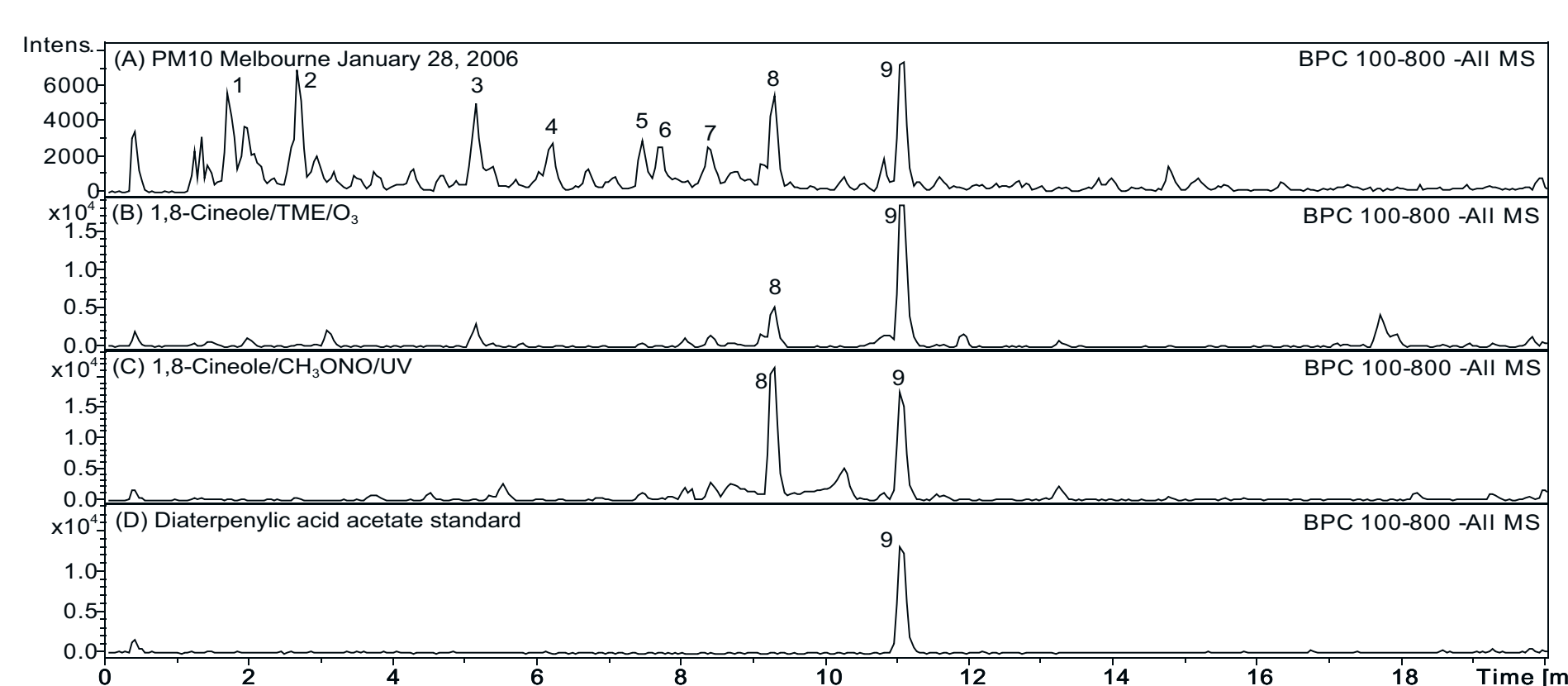

Figure 3. HPLC/ESI-TOFMS base peak chromatograms for (A) an ambient sample collected at Melbourne (B) a chamber sample collected from cineole/TME/ozone system (C) a chamber sample collected from cineole/NOx/UV system, and (D) diaterpenylic acid acetate reference compound. Peaks 8 and 9 are diaterebic acid acetate and diaterpenylic acid acetate
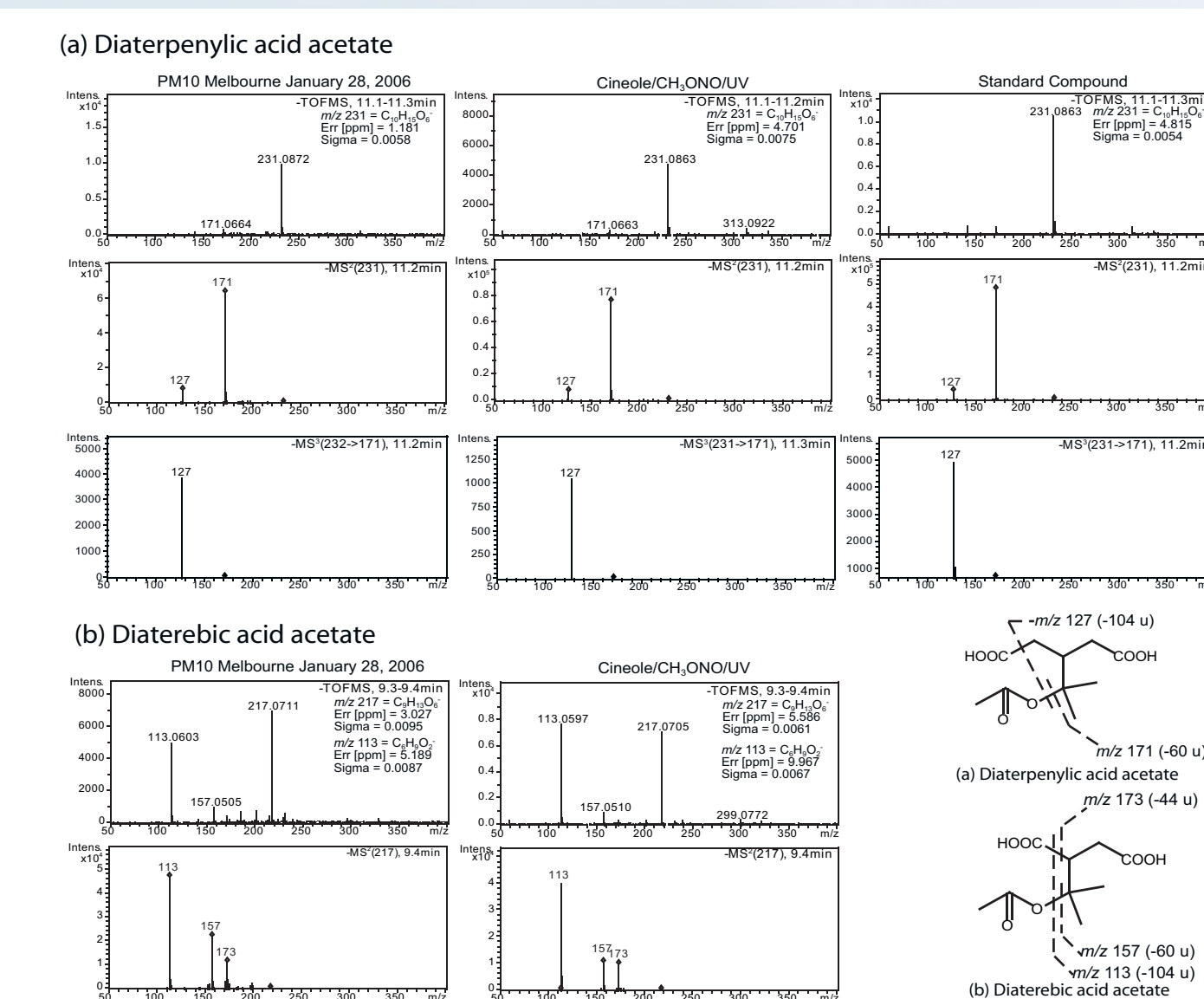

Figure 4. HPLC/ESI-TOFMS and ITMS^n mass spectra for (a) diaterpenylic acid actate and (b) diaterebic acid acetate
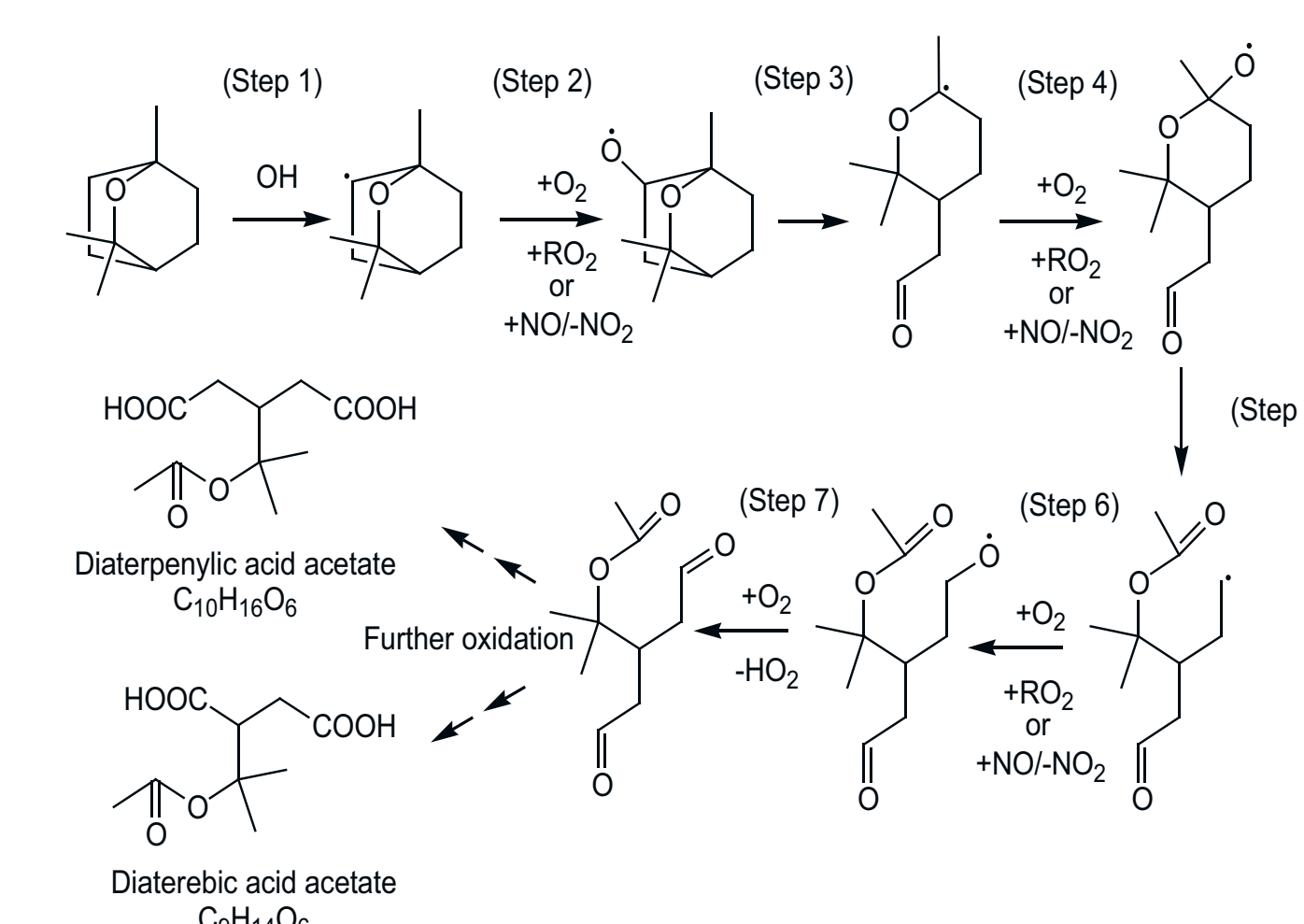

Figure 5. Proposed formation mechanisms for diaterebic acid acetate and diaterpenylic acid acetate

References

(1) Kanakidou, M. *et al.*, Organic aerosol and global climate modelling: a review, *Atmos. Chem. Phys.*, 2005, **5**, 1053
(2) Slee, A. *et al.*, *EUCLID: Eucalipts of Australia*; 3rd ed.; CSIRO PUBLISHING, Collingwood, **2006**
(3) Lungo, A. et al., Global planted forests thematic study: results and analysis. In *Planted Forests and Tree Working Paper*; FAO: Rome, **2006**; Vol. 38
(4) He, C.R. *et al.*, Monoterpene and isoprene emissions from 15 Eucalyptus species in Australia, *Atmos. Environ.*, 1996, **30**, 1437