

Supplementary Material

Mechanisms for the formation of secondary organic aerosol components from the gas-phase ozonolysis of α -pinene, Yan Ma, Andrew T. Russell and George Marston*.

Mass spectral data of the products identified from the gas-phase ozonolysis of α -pinene

The identification of α -pinene ozonolysis products was made using a ThermoFinnigan gas chromatograph with mass spectrometric detection (GC-MS) in electron impact (EI, 70eV) and negative chemical ionisation (CI(-), methane) modes following derivatisation using 14% BF₃/MeOH.

Names, molecular weights and chemical structures of the identified products are listed in Table 1.

cis-Pinic acid (as its dimethyl ester), *cis*-pinonic acid (as its methyl ester) and pinonaldehyde (as its dimethoxy acetal) were identified by comparison of the GC retention times and mass spectra with those of the derivatised authentic standards. The EI and CI(-) mass spectra of these compounds in a product sample are shown in Figs. SP1–SP3. In order to facilitate spectral interpretation, these compounds were examined first as models for the mass fragmentation patterns.

The EI spectra of the methylated *cis*-pinic and *cis*-pinonic acids both contain fragment ions corresponding to loss of CH₃O, CH₃OH and CH₃O–CHO from the molecular ion that are characteristic of the carboxylic acid methyl esters. The EI MS of pinonic acid methyl ester is also characterized by an intense ion at *m/z* 43 derived from the fragment of acetyl group. The CI(-) mass spectra for both methylated acids are characterized by an intense *quasi*-molecular ion M–1, together with ion peaks at M–31 ([M–CH₃O][–]) and M–33 ([M–H–CH₃OH][–]). For pinic acid dimethyl ester, minor peaks are also observed at M–63 and M–65, which can be interpreted as a further loss of methanol from the M–31 and M–33 ions respectively. In addition, a clear *m/z* 73 peak is present in both CI(-) spectra; this can be assigned to the CH₂C(O)OCH₃ fragment on the side chain of both molecules. The above fragmentation patterns have been further verified using a number of other acid standards, *e.g.*, glutaric acid (HO(O)C(CH₂)₃C(O)OH), adipic acid

(HO(O)C(CH₂)₄C(O)OH), 5-oxoheptanoic acid (CH₃C(O)(CH₂)₃C(O)OH) and 6-oxohexanoic acid (CH₃C(O)(CH₂)₄C(O)OH).

Pinonaldehyde was detected as its dimethoxy acetal. Kawamura *et al.*^{1,2} have previously reported the derivatisation of ω-oxocarboxylic acids to dimethoxy acetal esters using 14% BF₃/methanol (100 °C for 30 min) and the conversion of aldehyde, carboxyl and keto groups to dibutyl acetal, dibutyl ester and dibutyl ketal respectively, using 14% BF₃/butanol (100 °C for 30 min). Due to the milder conditions used here (60 °C for 30 min), only the aldehyde group in pinonaldehyde was derivatised to acetal during work-up, while the keto group was not converted. The EI mass spectrum of the derivatised pinonaldehyde exhibits a strong peak at *m/z* 75 corresponding to the terminal acetal group CH(CH₃O)₂, and a strong signal from the acetyl group at *m/z* 43. The CI(−) mass spectrum contains a strong M−1 signal, and a few other fragments including M−31, M−33, M−63 and M−65, in accordance with the dimethoxy structure.

Reference standards are not readily available for the other products, but for methylated *cis*-norpinic and *cis*-norpinonic acids, Koch *et al.*³ have published EI mass spectra. A compound with a mass spectrum corresponding to that identified as *cis*-norpinic acid dimethyl ester elutes *ca.* 0.7 min earlier than *cis*-pinic acid dimethyl ester. Its EI and CI(−) spectra (Fig. SP4) are analogous to those of pinic acid dimethyl ester but show a number of features at 14 amu less than the corresponding peaks of that compound. The CI(−) mass spectrum shows no peak at *m/z* 73 (CH₂C(O)OCH₃) and also shows that this compound has a molecular weight of 200, thus confirming the interpretation of Koch *et al.* Similar comments can be made about the compound with an EI mass spectrum corresponding to what Koch *et al.* assigned as methylated *cis*-norpinonic acid; it elutes 0.8 min earlier than methylated *cis*-pinonic acid, does not show a peak at *m/z* 73, and has a molecular weight of 184, thus confirming Koch *et al.*'s assignment.

Mass spectral data for a compound eluting *ca.* 0.7 min earlier than pinonaldehyde dimethoxy acetal are shown in Fig. SP6. The EI spectrum shows peaks corresponding to CH₃CO (*m/z* 43) and CH(OMe)₂ (*m/z* 75), while the CI(−) spectrum shows that the compound has a molecular weight of 200, and a number of peaks at 14 amu less than the

corresponding peaks in the spectrum of pinonaldehyde dimethoxy acetal. We identify this compound therefore as norpinonaldehyde dimethoxy acetal.

Two aldehydic acids, norpinalic acid and pinalic-3-acid were tentatively identified as their corresponding dimethoxy acetal methyl esters. The retention time for methylated pinalic-3-acid is *ca.* 0.7 min longer than that for methylated norpinalic acid, which is consistent with the relationship between the two structures (see the retention times for methylated: pinic *vs.* norpinic acids; pinonic *vs.* norpinonic acids; and pinonaldehyde *vs.* norpinonaldehyde). The EI and CI(–) fragmentation patterns and assigned structures for these compounds are displayed in Fig. SP7 and SP8 respectively. Their EI mass spectra are analogous to the NIST reference spectrum of 5,5-dimethoxy-pentanoic acid methyl ester and the spectra reported by Kawamura *et al.*¹ for the BF₃/MeOH treated C₇–C₉ aldehydic acids, showing peaks at M–31 and M–63, and at *m/z* 75. Their CI(–) mass spectra contain intense *quasi*-molecular ion peaks at M–1, and fragments (M–31, M–33, M–63, M–65, M–95) from the sequential loss of three CH₃O or CH₃OH groups, consistent with the suggested structures. Note that two likely structures may be assigned to pinalic acid: pinalic-3-acid (2,2-dimethyl-3-formylmethyl-cyclobutylmethanoic acid) and pinalic-4-acid (2,2-dimethyl-3-formyl-cyclobutylethanoic acid). Koch *et al.*³ and Yu *et al.*⁴ suggested the formation of pinalic-3-acid in their α -pinene ozonolysis experiments, while Glasius *et al.*⁵ proposed the structure of pinalic-4-acid for a compound with the same molecular mass. For the compound detected in our study, the CI(–) spectrum shows no fragment ion of *m/z* 73 corresponding to CH₂C(O)OCH₃, indicating that the carboxylic group is not attached to the methylene group. Therefore the more likely structure for this compound is a cyclobutylmethanoic acid methyl ester, *i.e.* pinalic-3-acid methyl ester, rather than pinalic-4-acid methyl ester.

Two compounds were detected that each appeared to contain a hydroxyl group. A compound eluting close to *cis*-pinic acid dimethyl ester shows a very similar EI mass spectrum and the same MW as *cis*-pinic acid dimethyl ester (see Fig. SP9); however, its CI(–) mass spectrum gives a fragment ion at *m/z* 196 (M–18), which is not observed for pinic acid dimethyl ester. This fragment indicates the presence of at least one functional group that is able to give the loss of H₂O. A feature at *m/z* 73 points to the presence of

the $\text{CH}_2\text{C}(\text{O})\text{OCH}_3$ group, and based on these data the suggested structure for this compound is the methyl ester of 10-OH-pinonic acid.

Another hydroxy-carboxylic acid was identified with a longer retention time than 10-OH-pinonic acid. The combined EI and CI(-) mass spectral data (Fig. SP10) indicate that this compound is a dimethoxy acetal carboxylic acid methyl ester, with a molecular weight of 246 and the presence of one functional group able to produce the loss of H_2O . Based upon the spectral information and mechanistic considerations, this compound is therefore identified as 4-OH-pinalic-3-acid acetal ester, which is likely to be derivatised from 4-OH-pinalic-3-acid.

Table 1. Products identified from the gas-phase ozonolysis of α -pinene.

Product name	Molecular weight	Structure
Pinic acid ^a	186 deri.: 214	
Pinonic acid ^a	184 deri.: 198	
Pinonaldehyde ^a	168 deri.: 214	
Norpinic acid ^b	172 deri.: 200	
Norpinonic acid ^b	170 deri.: 184	
Norpinonaldehyde ^b	154 deri.: 200	
Pinalic-3-acid ^b	170 deri.: 230	
Norpinalic acid ^b	156 deri.: 216	
10-OH-pinonic acid ^b	200 deri.: 214	
4-OH-pinalic-3-acid ^b	186 deri.: 246	

^a Identification confirmed with authentic standard.

^b Tentatively identified. deri.: derivative.

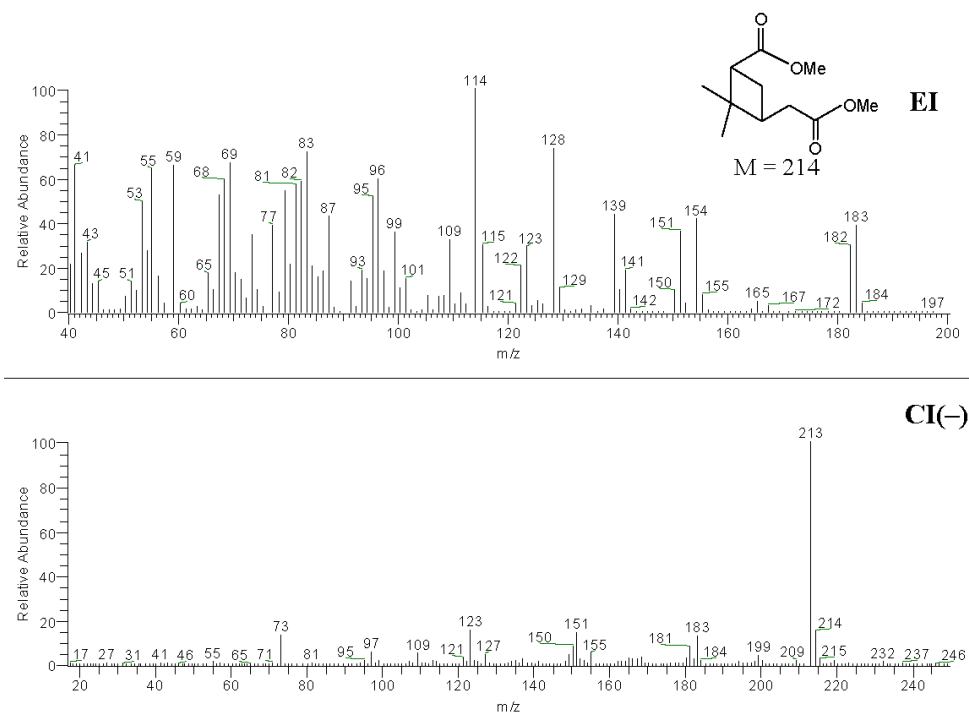


Fig. SP1: GC/EI and CI(-)-MS spectra for product peak identified as methylated *cis*-pinonic acid.

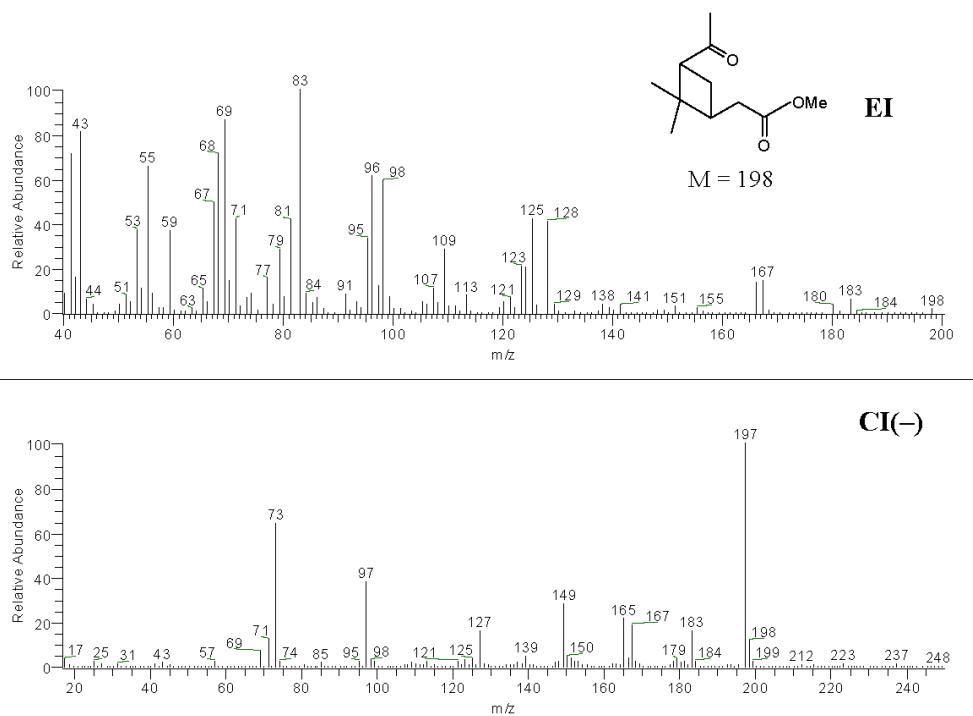


Fig. SP2: GC/EI and CI(-)-MS spectra for product peak identified as methylated *cis*-pinonic acid

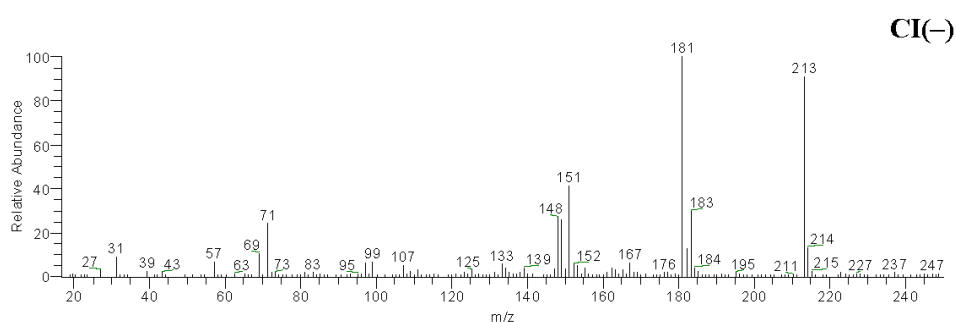
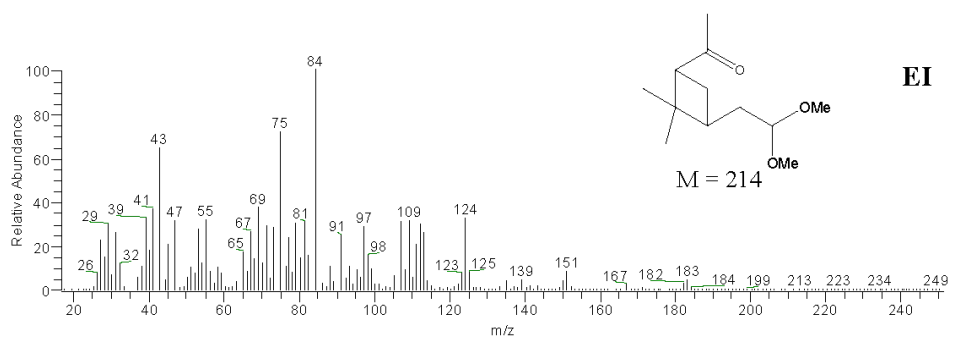


Fig. SP3: GC/EI and CI(-)-MS spectra for product peak identified as pinonaldehyde dimethoxy acetal.

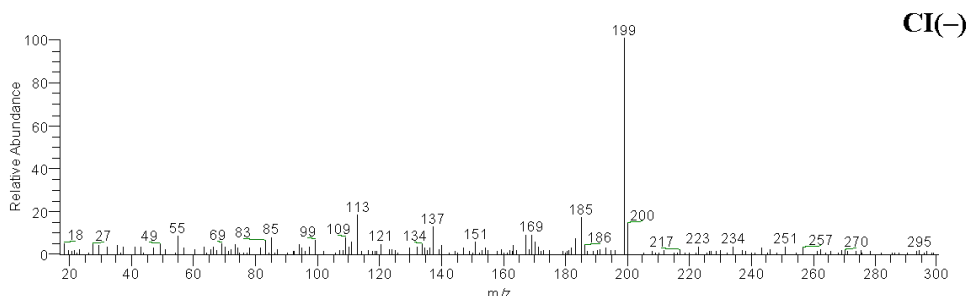
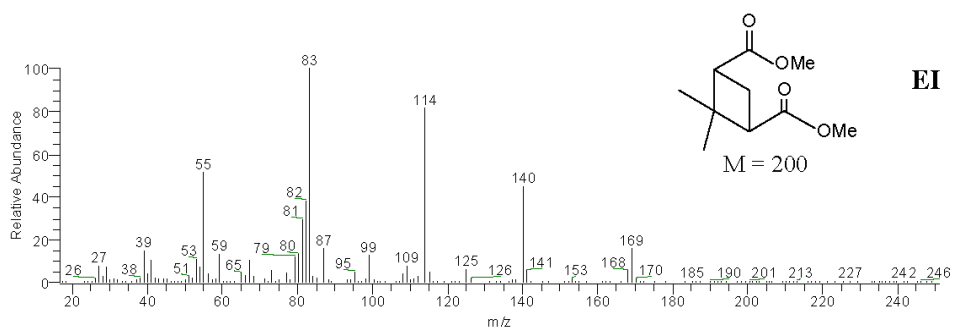


Fig. SP4: GC/EI and CI(-)-MS spectra for product peak tentatively identified as methylated norpinic acid.

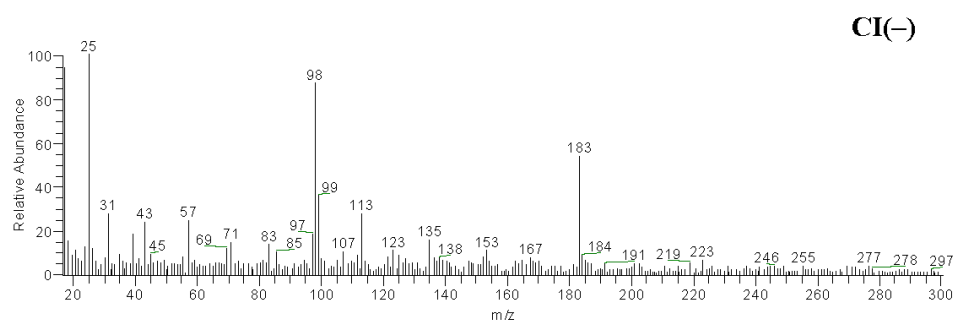
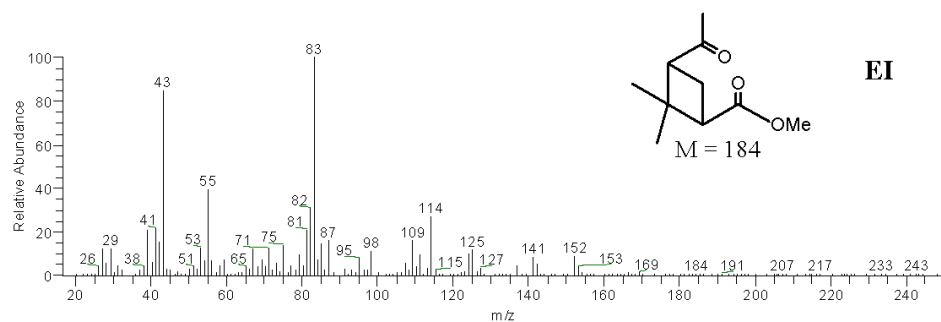


Fig. SP5: GC/EI and CI(-)-MS spectra for product peak tentatively identified as methylated norpinonic acid.

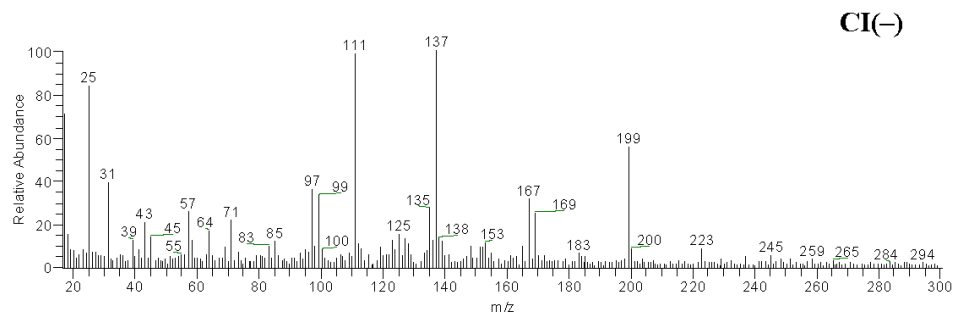
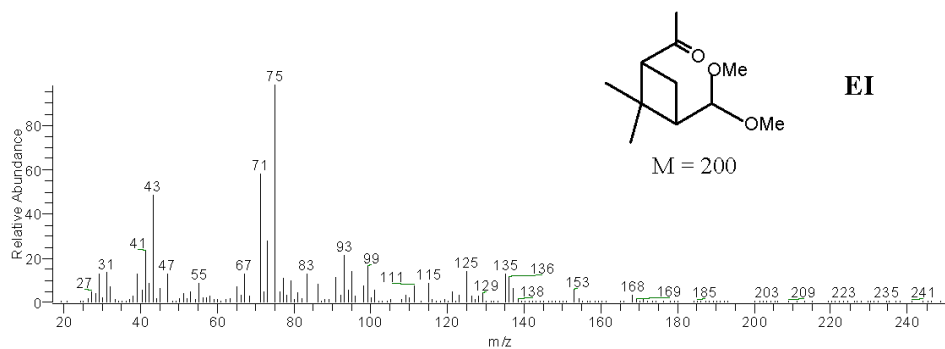


Fig. SP6: GC/EI and CI(-)-MS spectra for product peak tentatively identified as norpinonaldehyde dimethoxy acetal.

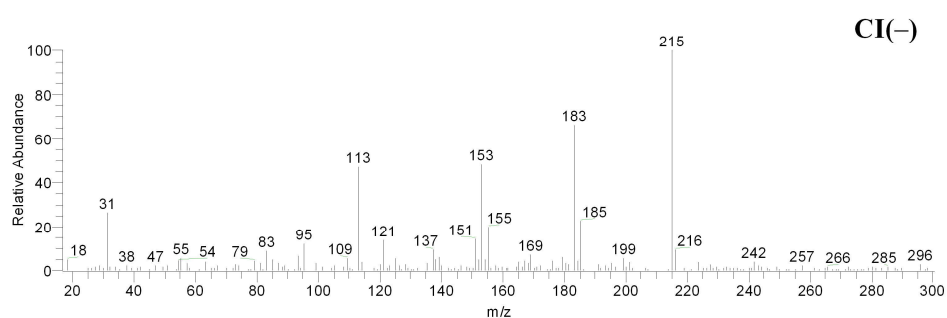
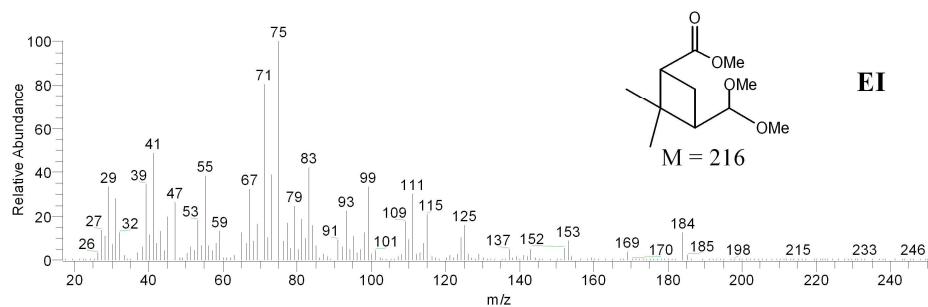


Fig. SP7: GC/EI and CI(-)-MS spectra for product peak tentatively identified as methylated norpinalic acid.

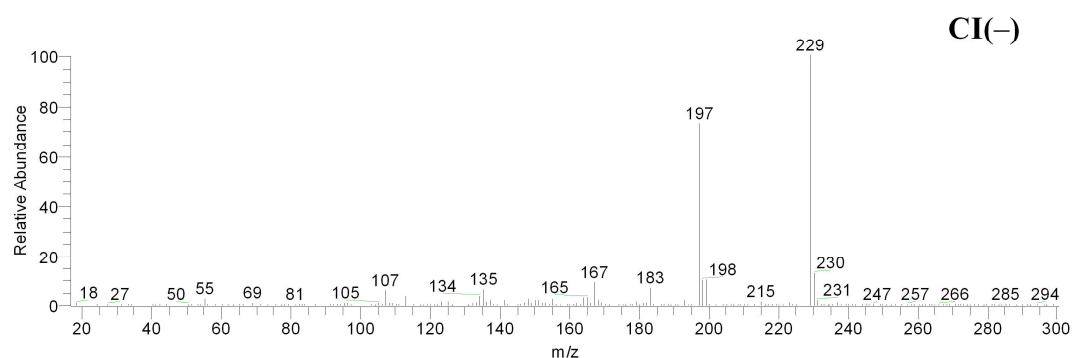
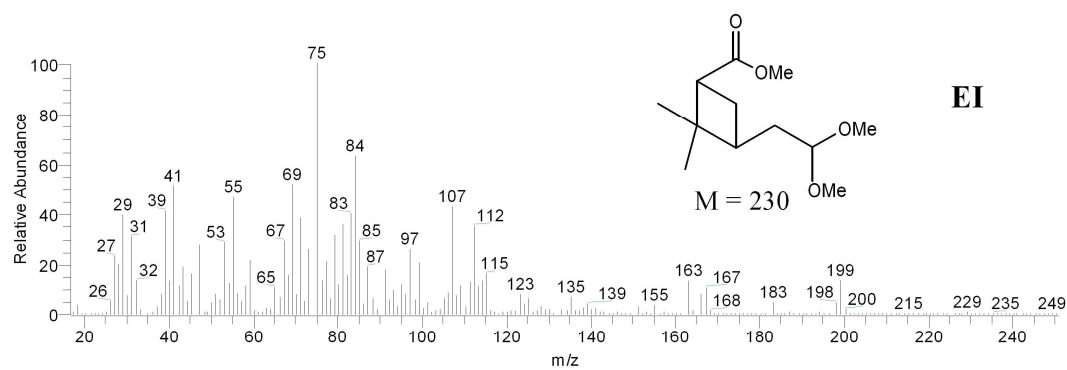


Fig. SP8: GC/EI and CI(-)-MS spectra for product peak tentatively identified as methylated pinalic-3-acid.

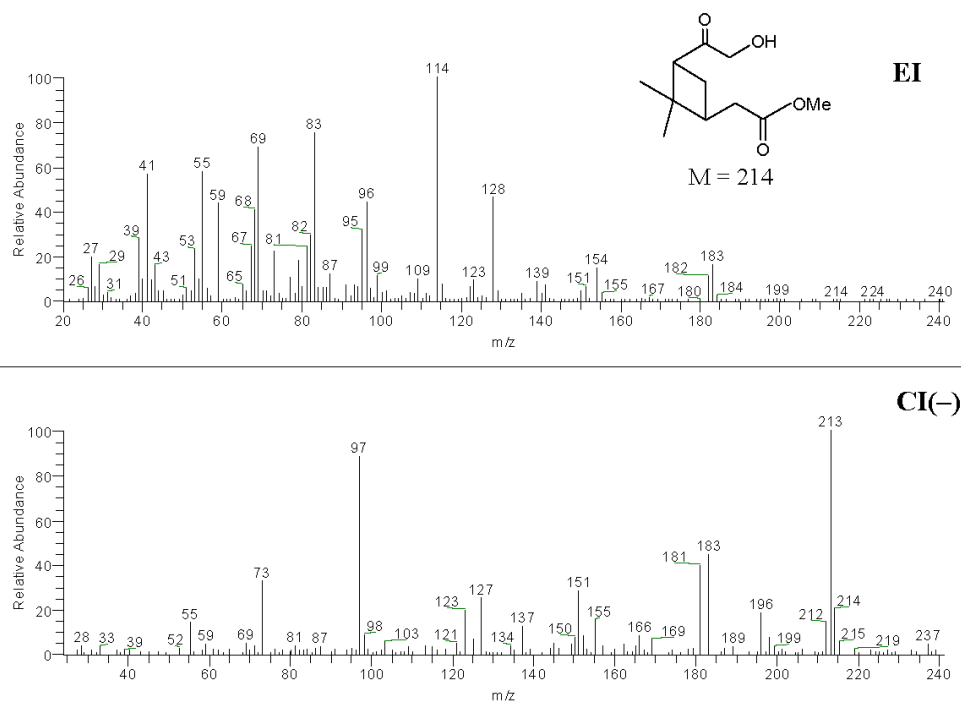


Fig. SP9: GC/EI and CI(-)-MS spectra for product peak tentatively identified as methylated 10-OH-pinonic acid.

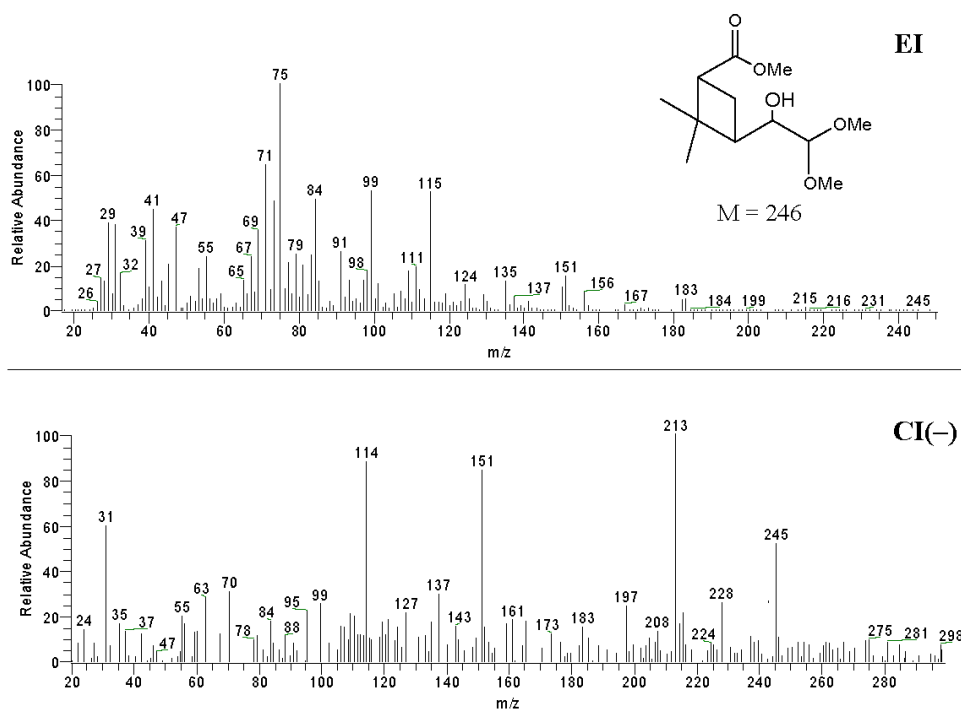


Fig. SP10: GC/EI and CI(-)-MS spectra for product peak tentatively identified as methylated 4-OH-pinalic-3-acid.

1. K. Kawamura and R. B. Gagosian, *J. Chromat.*, 1987, **390**, 371.
2. K. Kawamura, *Anal. Chem.*, 1993, **65**, 3505.
3. S. Koch, R. Winterhalter, E. Uherek, A. Kolloff, P. Neeb and G. K. Moortgat, *Atmos. Environ.*, 2000, **34**, 4031.
4. J. Yu, R. C. Flagan and J. H. Seinfeld, *Environ. Sci. Technol.*, 1998, **32**, 2357.
5. M. Glasius, M. Lahaniati, A. Calogirou, D. Di Bella, N. R. Jensen, J. Hjorth, D. Kotzias and B. R. Larsen, *Environ. Sci. Technol.*, 2000, **34**, 1001.