Supplementary Material 1

Mechanisms for the formation of organic acids in the gas-phase ozonolysis of 3-carene,
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Mass spectral data of the products identified from the gas-phase ozonolysis of 3-carene

The identification of the reported 3-carene 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.

Eight organic acids and two dicarbonyl compounds were identified as their corresponding
methyl ester and/or acetal derivatives. These compounds were 3-caric acid, 3-caralic acid,
3-caronic acid, nor-3-caric acid, nor-3-caralic acid, nor-3-caronic acid, OH-3-caronic acid,
OH-3-caralic acid, 3-caronaldehyde and nor-3-caronaldehyde; they are expected to be
present in their cis-form due to the original cis-structure of 3-carene. Since no authentic
standards are available, all these compounds were identified using their respective GC/EI
and CI(–) mass spectral data, as shown in Fig. SP1–SP10.

For the corresponding products identified from 3-carene and α-pinene ozonolysis, the
mass spectra indicate identical molecular weights and similar mass fragmentation
patterns that are characteristic of the methyl ester and/or dimethoxy acetal structures. For
compounds containing an acetyl group, the EI mass spectrum is also characterised by an
intense peak at \( m/z \) 43. Thus the spectral data of 3-carene products can be interpreted in
the same way as for our previously identified α-pinene ozonolysis products, described in
the supplementary material for ref. 1.
Fig. SP1: GC/EI and CI(−)-MS spectra for product peak identified as methylated cis-3-caric acid.

Fig. SP2: GC/EI and CI(−)-MS spectra for product peak identified as methylated cis-3-caralic acid.
Fig. SP3: GC/EI and CI(−)-MS spectra for product peak identified as methylated cis-3-caronic acid.

Fig. SP4: GC/EI and CI(−)-MS spectra for product peak identified as cis-3-caronaldehyde dimethoxy acetal.
Fig. SP5: GC/EI and CI(−)-MS spectra for product peak identified as methylated \textit{cis}-nor-3-caric acid.

Fig. SP6: GC/EI and CI(−)-MS spectra for product peak identified as methylated \textit{cis}-nor-3-caralic acid.
Fig. SP7: GC/EI and Cl(−)-MS spectra for product peak identified as methylated cis-nor-3-caronic acid.

Fig. SP8: GC/EI and Cl(−)-MS spectra for product peak identified as cis-nor-3-caronaldehyde dimethoxy acetal.

**Fig. SP9**: GC/EI and CI(−)-MS spectra for product peak identified as methylated *cis*-OH-3-caronic acid

**Fig. SP10**: GC/EI and CI(−)-MS spectra for product peak identified as methylated *cis*-OH-3-caralic acid