

## Supplementary Material 1

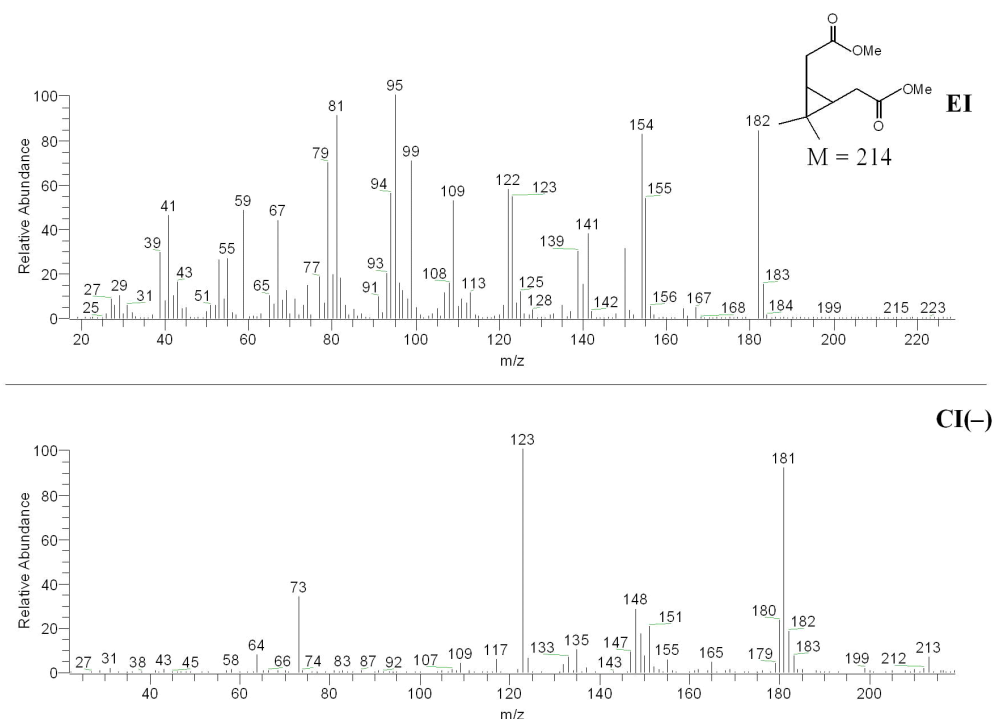
*Mechanisms for the formation of organic acids in the gas-phase ozonolysis of 3-carene*, Yan Ma, Rachel A. Porter, David Chappell, Andrew T. Russell and George Marston\*

### **Mass spectral data of the products identified from the gas-phase ozonolysis of 3-carene**

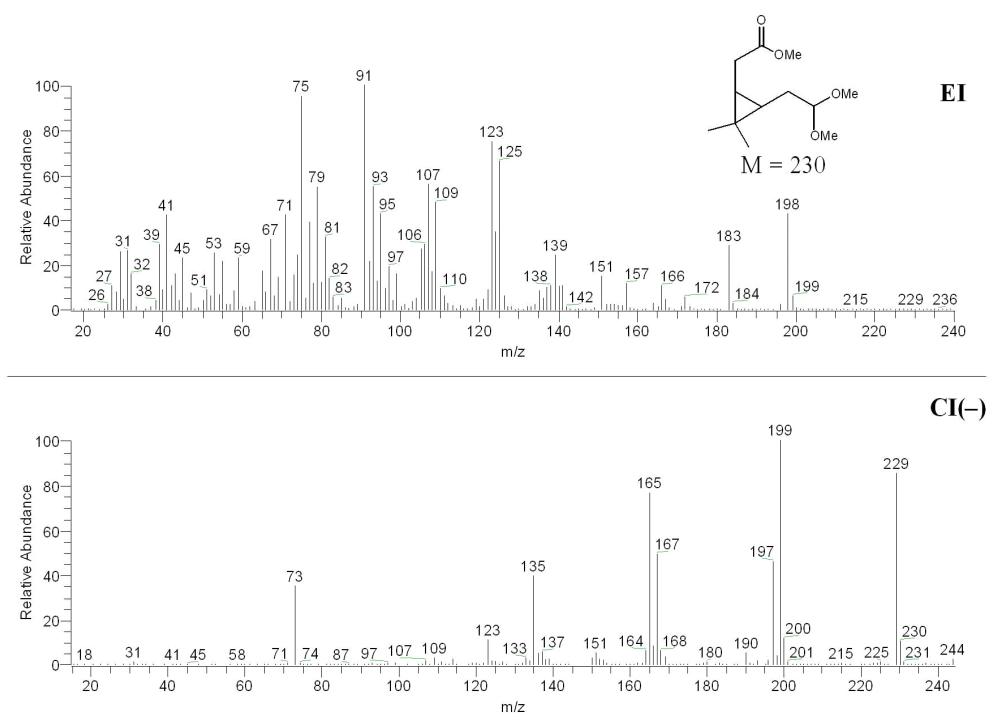
The identification of the reported 3-carene ozonolysis products was made using a ThermoFinnigan gas chromatograph with mass spectrometric detection (GC-MS) in electron impact (EI, 70eV) and negative chemical ionisation (CI(-), methane) modes following derivatisation using 14% BF<sub>3</sub>/MeOH.

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.

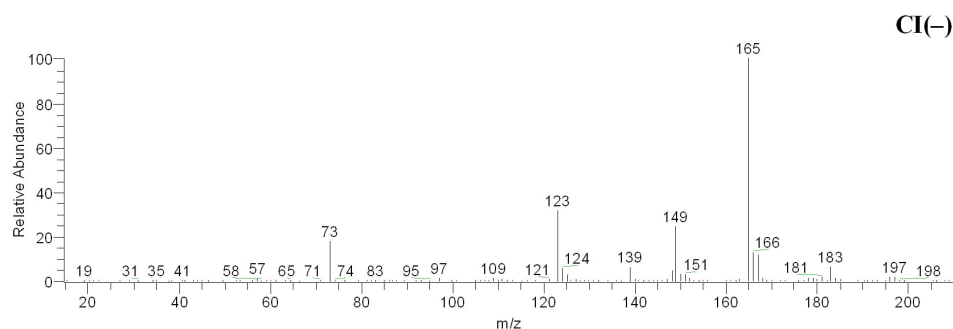
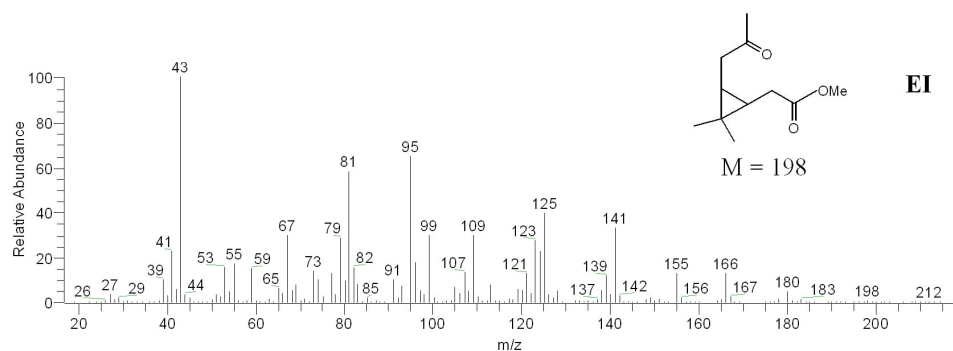
For the corresponding products identified from 3-carene and  $\alpha$ -pinene ozonolysis, the mass spectra indicate identical molecular weights and similar mass fragmentation patterns that are characteristic of the methyl ester and/or dimethoxy acetal structures. For compounds containing an acetyl group, 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  $\alpha$ -pinene ozonolysis products, described in the supplementary material for ref. 1.



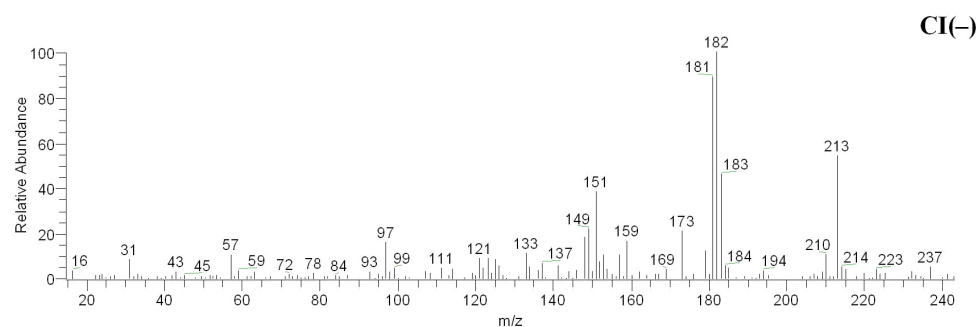
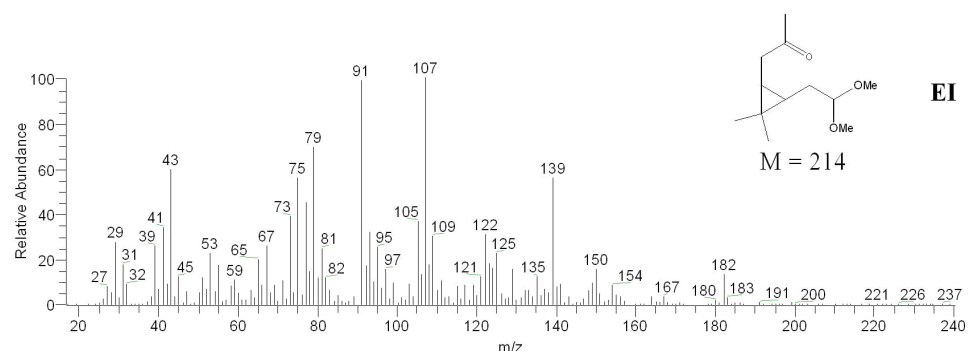
**Fig. SP1:** GC/EI and CI(-)-MS spectra for product peak identified as methylated *cis*-3-caric acid.



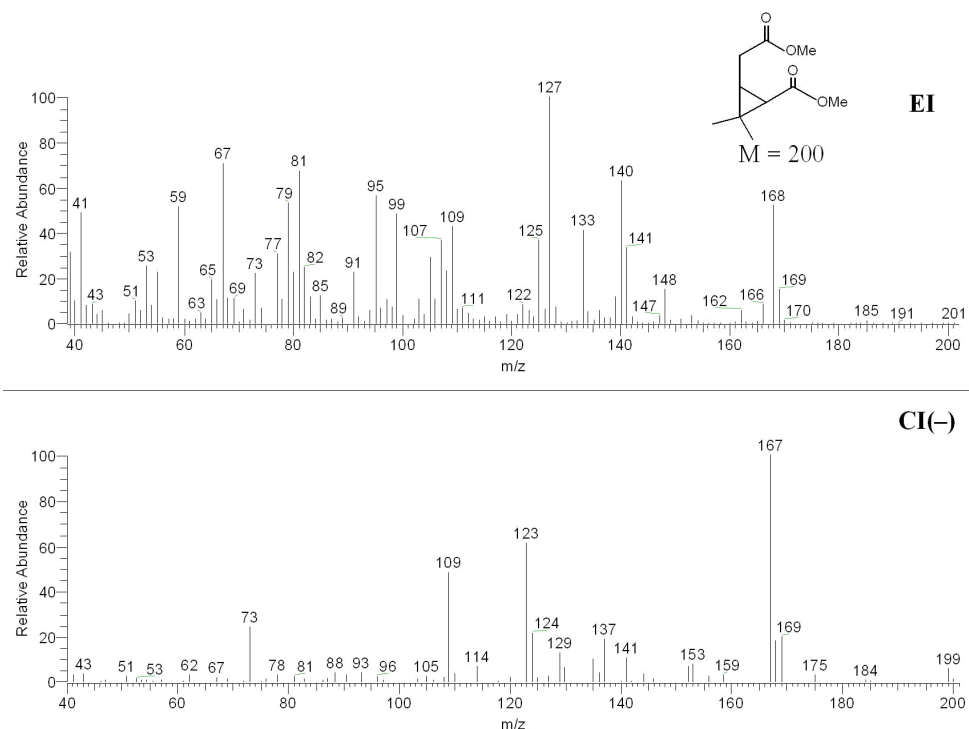
**Fig. SP2:** GC/EI and CI(-)-MS spectra for product peak identified as methylated *cis*-3-caralic acid.



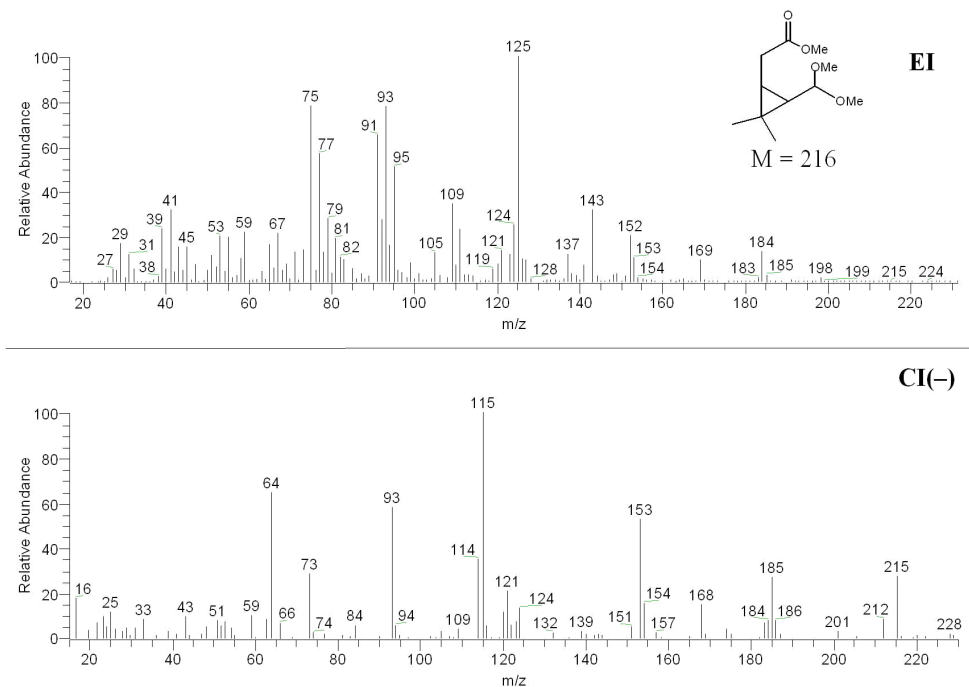
**Fig. SP3:** GC/EI and CI(-)-MS spectra for product peak identified as methylated *cis*-3-caronic acid.



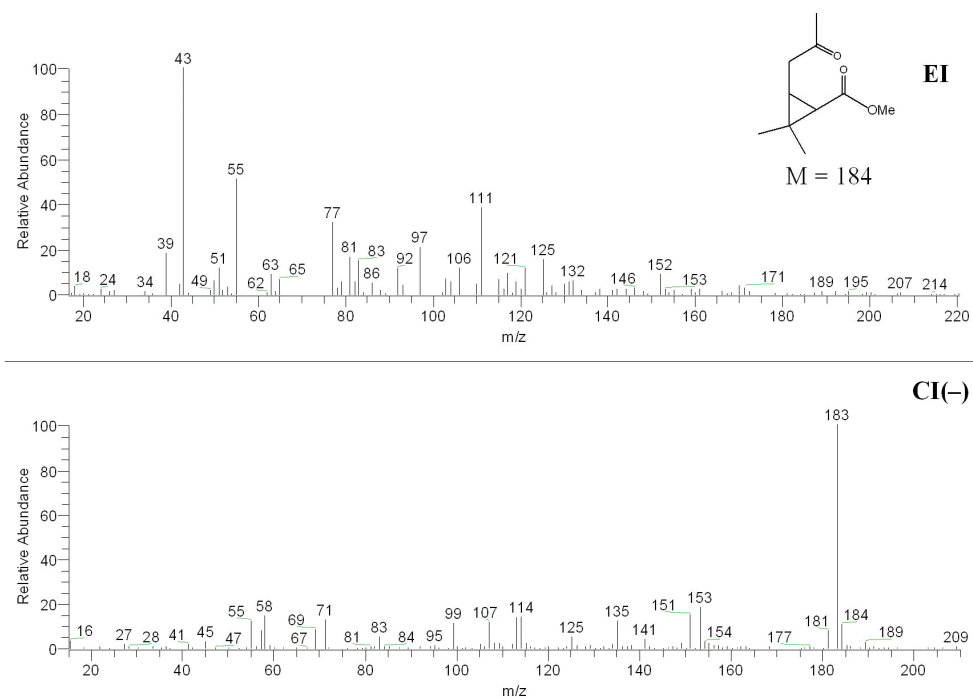
**Fig. SP4:** GC/EI and CI(-)-MS spectra for product peak identified as *cis*-3-caronaldehyde dimethoxy acetal.



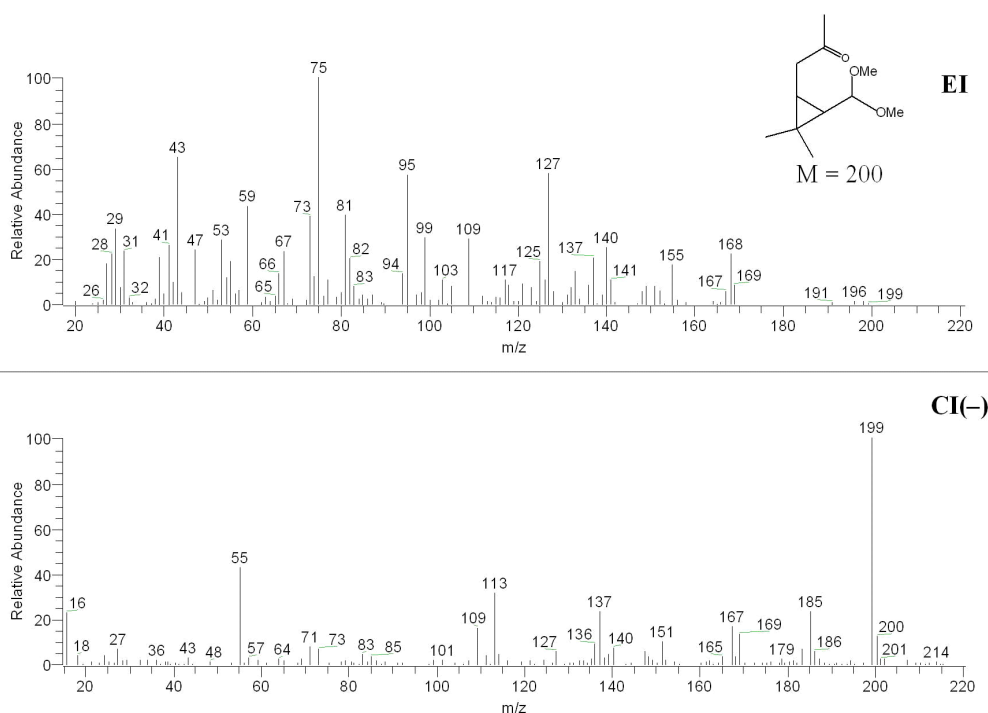
**Fig. SP5:** GC/EI and CI(-)-MS spectra for product peak identified as methylated *cis*-nor-3-caric acid.



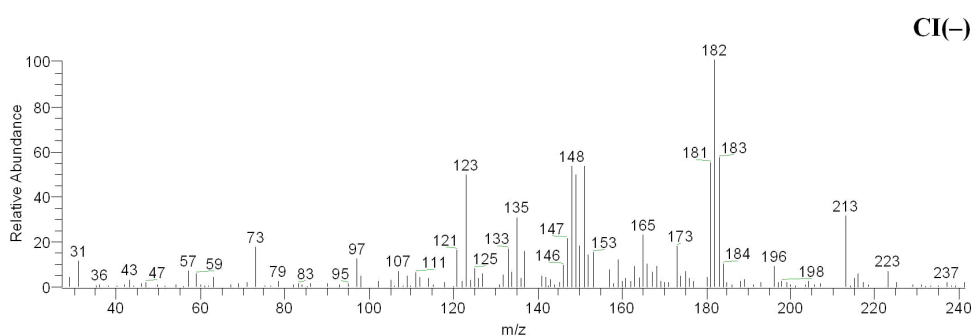
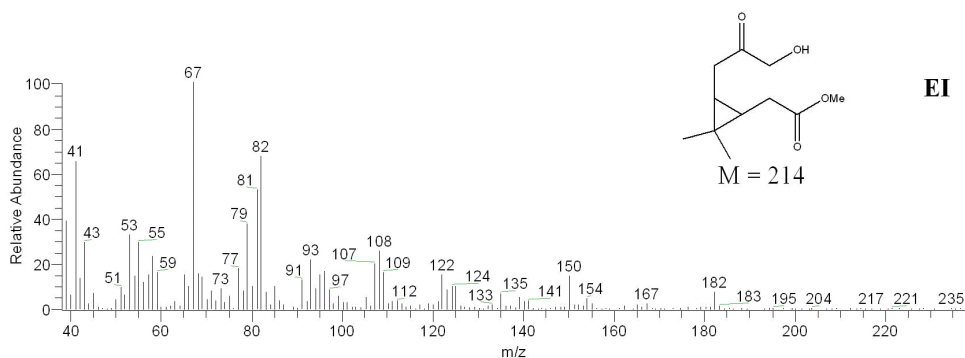
**Fig. SP6:** GC/EI and CI(-)-MS spectra for product peak identified as methylated *cis*-nor-3-caralic acid.



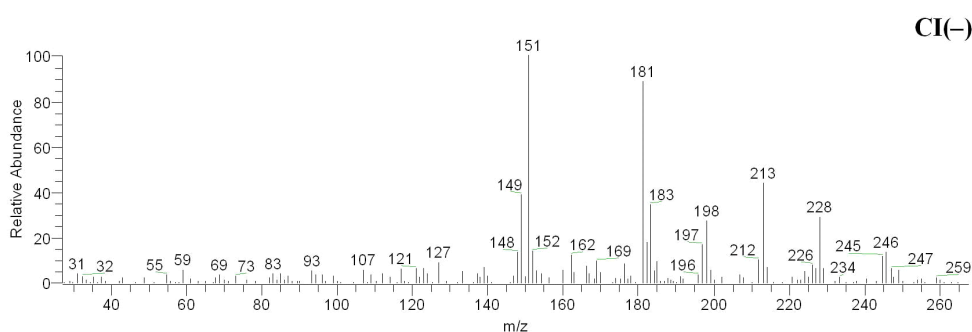
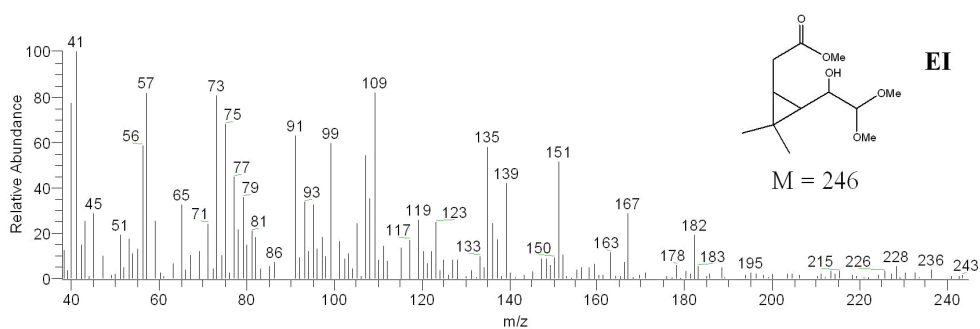
**Fig. SP7:** GC/EI and CI(-)-MS spectra for product peak identified as methylated *cis*-nor-3-caronic acid.



**Fig. SP8:** GC/EI and CI(-)-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

1. Y. Ma, A. T. Russell and G. Marston, *Phys. Chem. Chem. Phys.*, 2008, **10**, 4294.