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Spore chemistry as a proxy for UV-B flux

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Placing current increased terrestrial UV-B fluxes, due to the seasonal depletion of the stratospheric ozone layer, in a historical context is difficult due to a lack of long-term (century or more) instrumental records and necessitates developing proxy indicators. One promising line of enquiry derives from the response of plants to increased near-surface solar fluxes of harmful ultraviolet radiation in the 280 – 315 nm wavelength (UV-B) (Rozema et al. 2001, 2002). Plants exposed to increased UV-B radiation typically experience a number of detrimental effects, including damage to proteins, membrane lipids and DNA. To reduce this damage, many plants, animals and microbes accumulate UV-B protecting pigments (Cockell & Knowland 1999; Rozema et al. 2001, 2002).

Here, we evaluate the potential of a promising candidate for such a proxy, which is based on changes in the chemical composition of spores in response to variations in near-surface UV-B fluxes, in a field setting. We obtained spores from five populations of the tropical lycopsid *Lycopodium cernuum* growing across an altitudinal gradient (650-1981 m a.s.l.) in S.E. Asia with the assumption that they experienced a range of UV-B radiation doses. Spores from each population were analyzed for UV-B protecting compounds using micro-Fourier transform infrared spectroscopy (micro-FTIR) and thermochemolysis-GC-MS.

The data reveal the presence of various functional groups associated with UV-B protecting pigments including OH, C=O and C=C. Thermochemolysis and subsequent pyrolysis liberated UV-B pigments (ferulic and *para*-coumaric acid) from the spores. All of the aromatic compounds liberated from spores by thermochemolysis and pyrolysis were active in UV-B protection. We show systematic increases in micro-FTIR aromatic absorption

(1520 cm^{-1}) and olefinic or aromatic absorption (829 cm^{-1}) with altitude that reflect a chemical response to higher UV-B flux. Our results indicate that detailed chemical analyses of historical spore samples could provide a proxy for stratospheric O_3 layer variability and UV-B flux over historical (century to millennia) timescales.

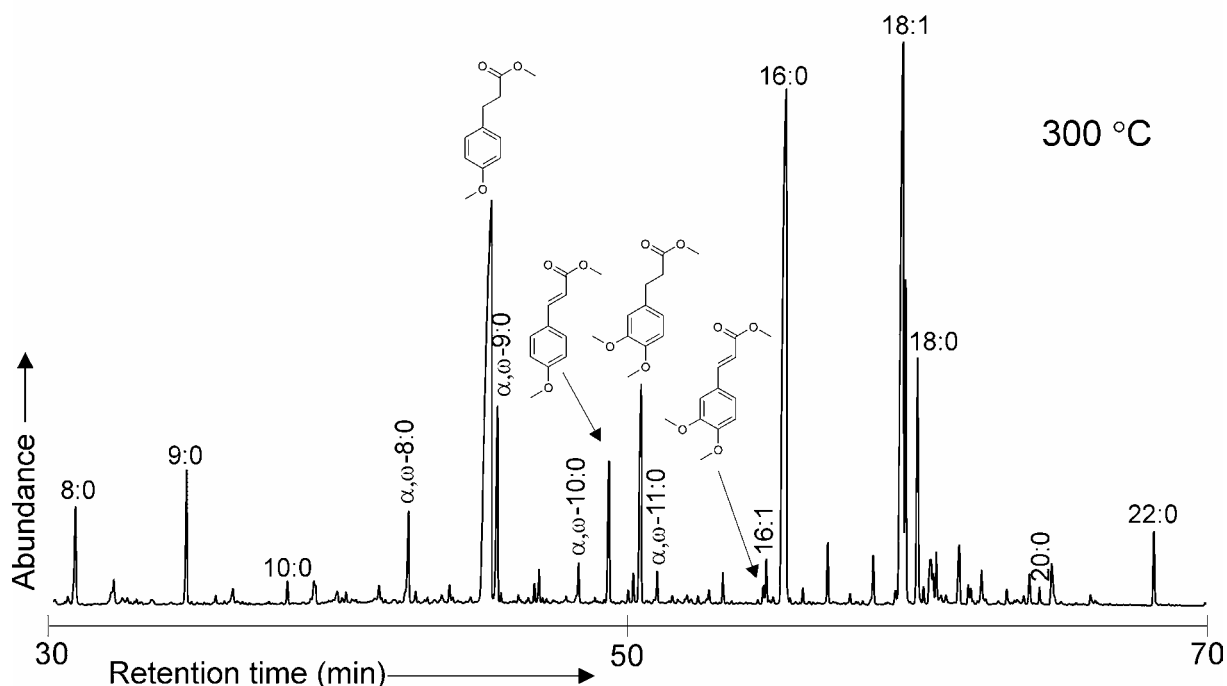


Figure 1: Total ion chromatogram of products from a typical *Lycopodium cernuum* sample liberated at 300 °C in the presence of TMAH

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