PLANT SUNSCREENS IN NATURE: UV AND IR SPECTROSCOPY OF SINAPATE DERIVATIVES

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Plants are exposed to prolonged amounts of UV radiation, with elevated levels of UV-B (280-320 nm) as the ozone layer is depleted. When UV-B radiation penetrates the leaf epidermis, substantial oxidative damage can occur to plant tissues and plant growth can be inhibited.[a] Sinapate esters, particularly sinapoyl malate, have been shown to efficiently prevent such damaging effects. By studying a series of molecules in this unique class under the isolated, cold conditions of a supersonic expansion, the fundamental UV-spectroscopic properties and photophysical aspects following UV absorption can be interrogated in detail. Sinapic acid and neutral sinapoyl malate were brought into the gas phase by laser desorption and detected via resonant two-photon ionization (R2PI). IR-UV double resonance methods were employed to obtain single-conformation UV and IR spectra. As the UV chromophore of interest is the sinapoyl moiety, sinapic acid served as the simplest model to compare directly to the more functionalized sinapoyl malate. It has a spectrum much like most aromatics, with a strong $\pi\pi^*$ origin, and well-resolved vibronic structure. By contrast, the spectrum for sinapoyl malate displays a large, broad absorption with little resolved vibronic structure, reflecting its role in nature as a pivotal and efficient UV protectant for plants, serving as the plants sunscreen. Using conformer-specific IR spectroscopy, the individual conformations of both species were assigned and used as the basis for further *ab initio* calculations of the excited states that give rise to the observed behavior.

[a] Landry, L.G.; Chapple, C.S.; Last, R.L. *Plant Physiol.* **1995**, *109*, 1159-1166.