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(I) Monitoring Humulone Isomerization Using Raman Spectroscopy: A Bitter Problem in the Microbrewing Industry

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Raman Spectroscopy is being explored to improve the characterization of beer bitterness which is derived primarily from the addition of the annual flowers (cones) of the perennial climbing vine Humulus lupulus (common hops). The hops cones contain humulones which are thermally isomerized into isohumulones during the brewing process. The isohumulones are highly bitter and contribute to the beer's flavour profile. Despite significant contributions to beer flavour and quality, humulone isomerization is not typically monitored in microbreweries because of the associated high cost. Raman spectroscopy probes molecular vibrations and, as such, is a potential low-cost analytical tool for the identification and quantification of specific molecules of interest in plants and food. In this work, the humulone isomerization process was mimicked using mixtures of pure humulone and isohumulone extracts, from 0% isomerization (i.e. pure humulone) to 100% isomerization (i.e. pure isohumulone).The Raman spectroscopy system consisted of an 830 nm laser (B&W Tek) coupled to a filtered fiber-optic probe (InPhotonics) and a spectrometer (Andor Technology) coupled to a deep-depletion CCD detector (Princeton Instruments). Two univariate methods for monitoring humulone isomerization were examined. In the first method, the integrated Raman peak intensity ratio 345-500cm-1/1668cm-1 decreased linearly with increased percent isomerization. In the second method, a continuous Raman peak shift from 624 cm-1 to 609 cm-1 was observed as the percent isomerization increased. Results are also compared to simulated Raman spectra for humulones and isohumulones obtained using density functional theory. The results demonstrate the ability of Raman spectroscopy to detect different concentrations of isohumulones in the presence of humulones under ideal conditions. The next step is to measure the thermal isomerization of humulone samples. The overall goal of this research is to develop a field-ready, cost-effective Raman spectroscopy technique for monitoring and optimizing beer flavour and quality.

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