Comparative Spectroscopic Analysis of Bee Propolis: NIR, FT-IR, FT-Raman and ^{1}H NMR. Focus on Provenance and Antioxidative Correlation

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Abstract

Propolis is a polyphenol-rich resinous substance well known for its antioxidative properties. This study describes and compares the chemical composition of propolis from Australia (N = 8), Denmark (N = 38), and Norway (N = 7) using Infrared (IR), Raman, Near-infrared (NIR), and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and correlates these findings with its Radical Scavenging Activity (RSA) through multivariate data analysis. IR, Raman, and NIR spectra were recorded from raw propolis, while ^{1}H NMR spectra were recorded on chloroform extracts. Results from Principal Component Analysis (PCA) showed that Danish and Norwegian propolis samples had a higher content of aromatic compounds compared to Australian samples, which in contrast were richer in carbohydrates and terpenoids. The RSA of Danish and Norwegian propolis samples were similar ($p \geq 0.05$), while the Australian samples exhibited significantly lower RSA. Correlation between selected spectral signals across the employed spectroscopic techniques and RSA was performed. The signals with the highest correlation value to RSA ($R^2 = 0.64$) were found at 1631 cm^{-1} (Raman) and 1666 nm (NIR), attributed to conjugated C=C stretching vibrations and first overtones of C-H stretching vibrations from aromatic/conjugated structures, respectively. Partial Least Squares (PLS) regression models based on each spectroscopic method revealed that the NIR-based predictions of the RSA had the highest accuracy, with R^2 and Root Mean Square Error of Cross-validation (RMSECV) values of 0.75 and 6.66 %, respectively.