

Comparative ^1H NMR Metabolomics between Scandinavian Propolis and Australian Propolis: The Quest to Identify Radical Scavenging Compounds

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Abstract

Propolis from *Apis mellifera* and cerumen from *Tetragonula carbonaria* are complex mixtures of beeswax, plant resins, and bee secretions whose composition varies with geography and species. Understanding these differences is important for exploring their bioactive potentials. This study employ untargeted quantitative ^1H NMR metabolomics to characterize *A. mellifera* propolis from Scandinavia (Denmark and Norway) and Australia, as well as cerumen from *T. carbonaria* in Australia. Hydrophilic and hydrophobic extracts were analyzed to assess compositional differences across geographical origin and bee species, and to link specific metabolites to radical scavenging activity (RSA).

Principal component analysis (PCA) of the spectra was readily able to separate Scandinavian from Australian propolis. Hydrophilic extracts showed that Scandinavian propolis contain higher levels of aromatic compounds, whereas Australian propolis are richer in carbohydrates. In contrast, cerumen from *T. carbonaria* exhibit higher amounts of terpenoids. Hydrophobic extracts revealed that Australian propolis has the highest wax content, with shorter chains and more free fatty acids, while Scandinavian propolis display uniform wax structures and the highest aromatic content. Multivariate regression using recursive weighted partial least squares (rPLS) to RSA prediction highlighted signals attributable to ferulic acid and p-coumaric acid, which was confirmed by statistical total correlation spectroscopy (STOCSY).

These findings demonstrate the utility of quantitative ^1H NMR metabolomics for distinguishing botanical and geographic chemotypes of propolis and cerumen. The findings further show that Scandinavian propolis is more consistent with respect to metabolite composition compared to Australian samples, presumably reflecting differences in resin sources for foraging.