Combined direct analysis in real-time mass spectrometry (DART-MS) with analytical pyrolysis for characterization of Chinese crude propolis

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Abstract:

A combination of direct analysis in real-time mass spectrometry (DART-MS) with analytical pyrolysis comprising evolved gas analysis-mass spectrometry (EGA-MS) and heart-cut EGA-gas chromatography (GC)/MS was used for characterization of Chinese crude propolis samples. DART-MS allowed us to profile general whole chemical components in propolis including terpenoids. phenolic acids and esters, flavonoid aglycones, flavonoid glycosides, phenolic glycerides and hydrocarbons with their molecular weights in the range of 100 - 800. EGA-MS was used to investigate the thermal behaviors of main components observed by DART-MS. The results revealed three temperature zones for the releasing behaviors of main constituents: (1) vaporization of terpenoids within 120-160 °C, (2) vaporization of phenolic acids and flavonoid aglycones, and pyrolysis of some flavonoid glycosides and beeswax within 160-300 °C, (3) pyrolysis of some flavonoid glycosides, phenolic glycerides and beeswax within 300-550 °C. Based on extracted ion thermograms of flavonoids, it is clear that chrysin and tectochrysin existed only as aglycones, while pinocembrin, galangin, 2', 6'-dihydroxy-4'-methoxychalcone and naringenin existed as both aglycones and glycosides. According to temperature zones, heart-cut EGA GC/MS data clearly indicated that 43 components were identified for 3 crude propolis samples collected from different origins, and grouped into 7 classes: alcohols/phenols, aldehydes/ketones, terpenoids, phenolic acids and esters, flavonoids, hydrocarbons and others, Among them, terpenoids, phenolic acids and esters, and flavonoids were main bioactive classes. Terpenoids accounted for 43.5-82.1 % in zone A, and flavonoids accounted for 3.7-23.9 % in zone B and 5.2-46.5 % in zone C, showing their different origins. In addition, flavonoid aglycones and their glycosides also could be semiquantitatively analyzed separately by analytical pyrolysis techniques used. Flavonoid aglycones accounted for a majority of total flavonoids with its proportions more than 52.6-66.7 % in propolis samples. All the obtained results demonstrate that the combination of these methods is effective for profiling all main components in Chinese crude propolis.

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Frontier Labs Products used:

Multi-Shot Pyrolyzer EGA/Py-3030D, UADTM-2.5 N