

HUMAN FOLLICULAR WAX ESTERS: A MASS SPECTROMETRIC STUDY OF A COMPLEX BIOLOGICAL MIXTURE.

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The analysis of complex mixtures of biological wax esters (WEs) provides a challenge for mass spectrometry. Typically, EI mass spectrometry has been the preferred method, and in recent times capillary gas chromatography-mass spectrometry has been used with great success. Under EI conditions, wax esters give a number of diagnostic peaks for both the fatty acid and fatty alcohol moieties. For saturated species, the fatty alcohol portion of the WEs gives characteristic $[\text{OCOR}]^+$ and $[\text{CH}_2\text{CH}(\text{CH}_2)_n\text{CH}_3]^+$ ions, whereas for the fatty acids the $[\text{RCO}_2\text{H}_2]^+$ and $[\text{RCO}]^+$ ions are most diagnostic. For monounsaturated WEs, where the double bond is located in the fatty acid portion of the molecule, the $[\text{RCO}-1]^+$ peak is characteristic. Conversely, when the double bond is located in the alcohol part of the molecule, then the unsaturated $[\text{CH}_2\text{CH}(\text{CH}_2)_n\text{CH}_3]^+$ fragmentation ion becomes prominent. Clearly, GCMS has been a powerful tool for the structural elucidation of WEs in complex mixtures.

Relatively few studies have been reported concerning the use of electrospray ionization to characterize intact wax esters, due in part to the inherent insensitivity of this technique for neutral lipids. However, the addition of NH_4^+ ions to wax ester mixtures results in the formation of ammonium adduct $[\text{WE}+\text{NH}_4]^+$ ions under ESI conditions. Collision induced dissociation of the $[\text{WE}+\text{NH}_4]^+$ ions gives characteristic $[\text{RCO}_2\text{H}_2]^+$ ions, enabling the ester mixture to be studied using tandem mass spectrometry, specifically MRM and neutral loss experiments. Here we report the analysis of a complex mixture of human follicular wax esters by capillary gas chromatography-mass spectrometry, and then analysis of this complex mixture of WEs using electrospray ionization mass spectrometry techniques.