UNRAVELLING THE MYSTERY OF WOOL PHOTOYELLOWING THROUGH MASS SPECTROMETRIC CHARACTERISATION OF CHROMOPHORES

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Ultraviolet light induced photo-oxidation of proteins has been implicated in a diverse range of deleterious processes including hair damage, skin ageing, eye lens opacification, and crop damage. In the case of wool, exposure to UV-B radiation results in a gradual yellow discolouration of the fibres. This photoyellowing represents a serious impediment to the marketability of wool products. Yellow chromophore containing photo-oxidation products were directly characterised within the proteins of untreated photoyellowed wool fabric utilising a quasi-proteomic approach. Irradiated fabric was tryptically digested and the resultant peptide mixture separated by HPLC with monitoring at 400 nm utilised to separate yellow fractions. Peptides from these yellow fractions were sequenced using tandem mass spectrometric analysis, with characterisation of photo-modified residues. In total, eight chromophoric species were identified and located within known wool peptide sequences. Five tryptophan derived photo-modifications were characterised, namely hydroxytryptophan, formylkynurenine, hydroxyformylkynurenine, kynurenine and hydroxykynurenine. Three tyrosine derived modifications were characterised, namely dihydroxyphenylalanine, dityrosine, and a previously unreported modification consistent with a hydroxylated dityrosine residue. The majority of modified residues were identified in peptides derived from wool intermediate filament proteins, with others found in high-glycine tyrosine and inner root sheath associated proteins. The range of photo-oxidation products characterised provides valuable insight into photochemical pathways leading to protein photoyellowing and experimental evidence consistent with mechanistic theories implicating the hydroxyl radical as a principal causative agent of protein photo-oxidation.

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