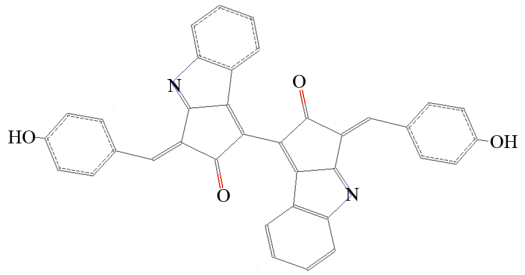
SCYTONEMIN FAMILY MOLECULES IN EXTREME ENVIRONMENTS: RAMAN SPECTROSCOPIC IDENTIFICATON AND DIFFERENTIATON . Tereza Varnali[1] and Howell G.M. Edwards[2], [1]Bogazici University, Department of Chemistry, Bebek 34342 Istanbul, Turkey. E-mail: varnali@boun.edu.tr, [2]Centre for Astrobiology and Extremophiles Research, School of Life Sciences, University of Bradford, Bradford, West Yorkshire BD7 1DP, UK. E-mail: H.G.M.Edwards@bradford.ac.uk

Introduction: Scytonemin is a cyanobacterial sheath pigment with potent UV (UV-A, UV-B and UV-C) absorbing properties[1] which has been spectroscopically well characterized[2,3]. Di- and tetramethoxy derivatives of scytonemin, scytonin and scytonemin-imine have also been found and described in the literature[4,5]. The importance of these biomolecules is their photoprotective function, which is one of the major survival strategies adopted by extremophiles in environmentally stressed conditions. The existence of the cyanobacterial stromatolitic colonies on early Earth, with the scytonemin protection afforded against radiation exposure in the early atmosphere and dating from about 3.5 Gya in our geological record, therefore could imply that such an occurance could have pertained on Mars[6]. Scytonemin has been identified as a prime biomarker in the search for extinct or extant life on planetary surfaces and subsurfaces. We established the molecular vibrational modes of the scytonemin family molecules and predicted theoretically their Raman spectra with the purpose of their recognition and differentiation both in terrestrial and extraterrestrial scenarios.



scytonemin

Scytonemin Family molecules: Apart from scytonemin, di- and tetramethoxy derivatives of scytonemin, scytonin and scytonemin-imine that have been isolated experimentally, hypothetical iron(III) complexes of scytonemin and its di- and tetramethoxy derivatives predicted by modeling and theoretical calculations are suggested to facilitate the movement of iron through the rock matrix[7,8,9]. A novel theoretically plausible, structure is proposed for oxidized scytonemin[10].

Computations: DFT calculations have been carried out at the B3LYP/6-31G** level for all optimizations and frequency calculations making use of the program package Gaussian09.

Conclusions: The theoretical analysis coupled with current Raman spectral observations of scytonemin in extremophilic cyanobacterial colonies illustrates the novel feature characteristic of some important reduced and oxidized forms, methoxy derivatives, iron complexes and the potential for their recognition in extreme scenarios. This work forms the basis for the establishment of diagnostic Raman spectral database for scytonemin and its derivatives, not only those which have already been reported in chemical extracts but which as yet have not been characterized spectroscopically, but also indicating potentially novel species which are predicted to be stable for cyanobacterial colonies in iron-rich environments [11] .

References: [1] Proteau P. J. et al. (1993) *Experientia,* 49, 825-829. [2] Edwards H.G.M. et al. (2000) *SAA,* 56, 193-200. [3] Varnali T. et al. (2009) *IJA,* 8, 133-140. [4] Bultel-Ponce V. et al. (2004) *J.Nat.Prod.,* 67, 678-681. [5] Grant C.S. and Louda J.W. (2013) *Org.Geochem.,* 65, 29-36. [6] Edwards H.G.M. et al. (2007) *JRS,* 38, 1352-1361. [7] Varnali T. and Edwards H.G.M. (2010) *Astrobiology*, 10, 711-716. [8] Varnali T. and Edwards H.G.M. (2013) *Astrobiology*, 9, 861-869. [9] Varnali T. and Edwards H.G.M. (2013) *PSS*, 82-83, 128-133. [10] Varnali T. and Edwards H.G.M. (2014) *SAA,* 117, 72-77. [11] Varnali T. and Edwards H.G.M. (2014) *PTRSA*, 372, 20140197.