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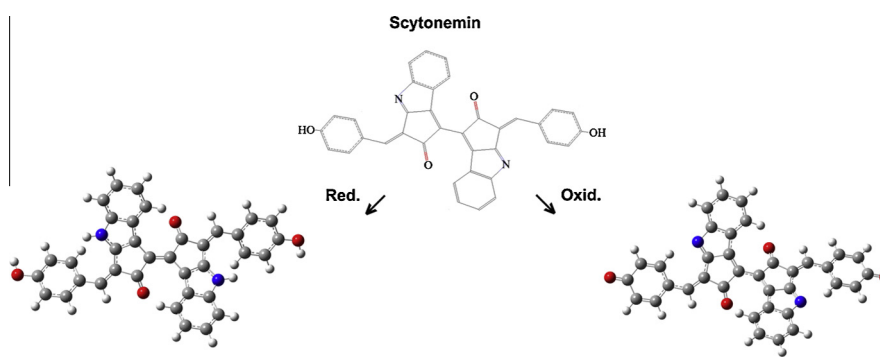
Reduced and oxidised scytonemin: Theoretical protocol for Raman spectroscopic identification of potential key biomolecules for astrobiology

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HIGHLIGHTS

- We propose a new, theoretically plausible structure for oxidised scytonemin.
- DFT calculations for scytonemin, red-scytonemin and the new oxid-scytonemin are done.
- Their theoretical Raman spectroscopic data and λ_{\max} UV-absorption data is presented.
- Vibrational spectroscopic assignments allow them to be detected and identified.
- We propose a protocol for their analytical discrimination.

GRAPHICAL ABSTRACT



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ABSTRACT

Scytonemin is an important UV-radiation protective biomolecule synthesised by extremophilic cyanobacteria in stressed terrestrial environments. Scytonemin and its reduced form have been both isolated experimentally and the Raman spectrum for scytonemin has been assigned and characterised experimentally both in extracts and in living extremophilic cyanobacterial colonies. Scytonemin is recognised as a key biomarker molecule for terrestrial organisms in stressed environments. We propose a new, theoretically plausible structure for oxidised scytonemin which has not been mentioned in the literature hitherto. DFT calculations for scytonemin, reduced scytonemin and the new structure modelled and proposed for oxidised scytonemin are reported along with their Raman spectroscopic data and λ_{\max} UV-absorption data obtained theoretically. Comparison of the vibrational spectroscopic assignments allows the three forms of scytonemin to be detected and identified and assist not only in the clarification of the major features in the experimentally observed Raman spectral data for the parent scytonemin but also support a protocol proposed for their analytical discrimination. The results of this study provide a basis for the search for molecules of this type in future astrobiological missions of exploration and the search for extinct and extant life terrestrially.

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Introduction

The discovery of scytonemin in extracts from cyanobacterial colonies harvested from the Antarctic Dry Valleys and the recognition of its fundamental role in the protection of organisms against intense low wavelength high energy solar insolation [1–3]

launched a series of papers which, following its first Raman spectroscopic characterisation [4], described its presence in a range of extremophilic scenarios [5–9]. Uniquely synthesised by cyanobacterial sheaths [10] in response to ambient radiation, the special highly conjugated aromatic structure of scytonemin [11] was found to be admirably suited for the removal of ultraviolet radiation in all UV-A, UV-B and UV-C regions of the electromagnetic spectrum, so affording the cyanobacteria excellent protection against the damaging effects of low wavelength radiation especially at wavelengths below 250 nm where DNA is destroyed [12]. Scytonemin has been found in over 300 species of cyanobacteria and the scytonemin biosynthetic gene cluster is highly conserved across cyanobacterial lineages [13]. The synthesis of scytonemin in the laboratory [14] was only reported as recently as 2011; hitherto, isolated extracts from cyanobacterial colonies have revealed the presence of substituted dimethoxy- and tetramethoxy-scytonemins [15,16], which, unlike the parent scytonemin, have yet to be characterised analytically in living colonies in the geological record.

The analytical spectroscopic characterisation of scytonemin demonstrated its molecular dimeric character, whose structure according to published *ab initio* calculations [17] is nonplanar due to steric hindrance effects and necessary for it functioning as a radiation protectant; the methoxy substituted congeners of scytonemin have also been studied theoretically [18] and have been shown to possess an exceptional aptitude for protection against low wavelength radiation. As yet, however, despite their being characterised in chemical extracts these methoxylated derivatives have not been identified *in situ* analytically in natural specimens of extremophilic cyanobacterial colonies. Similarly, efforts have recently been made to identify the spectral signatures [19] of iron-complexed scytonemin molecules, which are predicted to occur

as stable entities in cyanobacterial colonies exposed to an iron-rich terrestrial environment such as Rio Tinto near Huelva, Spain, where extremely low pH conditions created by the biological colonisation have mobilised the iron (III) and the role of scytonemin complexes in this process have yet to be evaluated experimentally; in this respect, the existence of scytonemin analogues in the iron-rich Martian regolith affords a relevant astrobiological comparator [20].

It is essential that the current database of key biomolecules produced by extremophilic organisms under severely stressed conditions terrestrially, especially for the carotenoids and scytonemin [21,22], is expanded to include chemical variants of some major protectants such as carotenoids and scytonemin; hence, the recognition of the possible existence of stable reduced and oxidised forms of scytonemin is potentially critical for the future detection of these in anaerobic or aerobic sites and in reduced and oxidised environments on Earth. The astrobiological relevance of this exercise to the viability of future detection of such oxidised and reduced analogues of scytonemin extraterrestrially is immediately apparent in for example, the highly oxidised surface regolith on Mars where the presence of significant quantities of peroxides and perchlorates have been detected by NASA rovers. In contrast, the reducing conditions at the surface of Titan detected in the Cassini mission could perhaps be harbouring the reduced form of scytonemin; clearly, it is vital for future spectroscopic instruments on search for life astrobiological missions to have the ability to recognise materials such as these.

The purpose of this paper is to investigate for the first time the theoretical possibility of existence of reduced and oxidised forms of scytonemin, to assess their protective capabilities for cyanobacterial organisms against high energy low wavelength radiation insolation relative to the parent scytonemin, and finally to predict

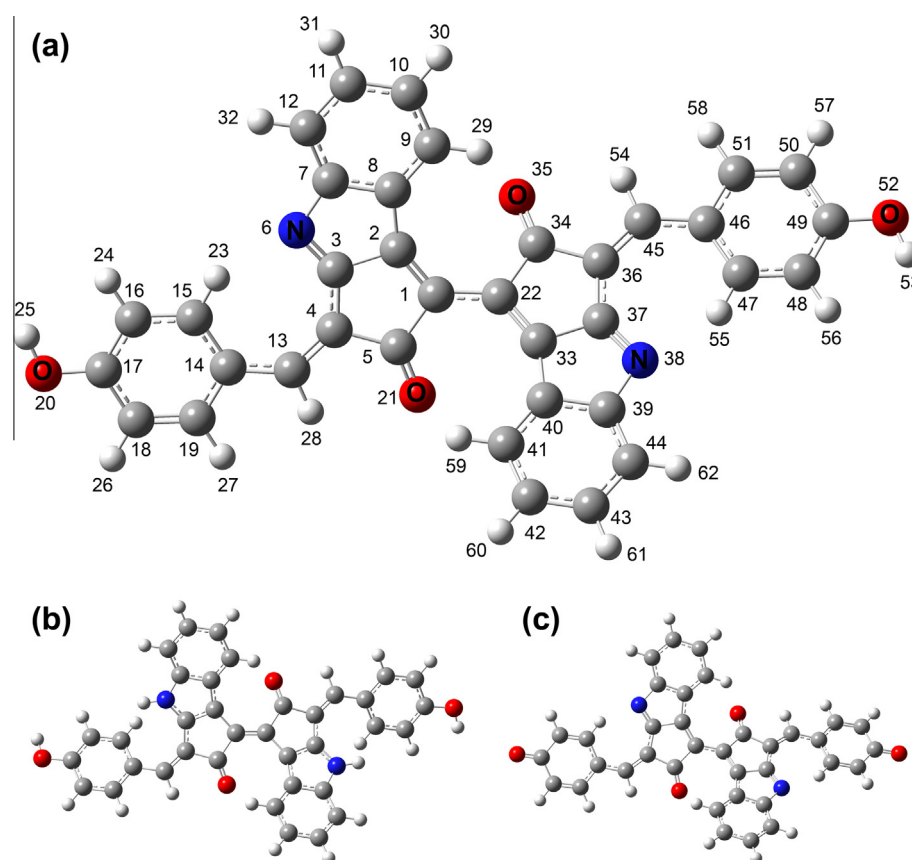


Fig. 1. Structures for (a) scytonemin (with numbering used in 'Computation', 'Results and discussion' and Table 2). (b) red-scytonemin, and (c) Oxid-scytonemin.

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