



Solar radiation exposure of dihydrobiopterin and biopterin in aqueous solution

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Abstract

Dihydrobiopterin (H₂Bip) and biopterin (Bip) accumulate in the skin of patients suffering from vitiligo, whose lack of melanin causes a deficient protection against UV radiation. H₂Bip and Bip undergo photooxidation upon UV irradiation and the former acts as a photosensitizer of biomolecules. The aim of this work is to study the photochemical reactions of these compounds triggered by sunlight under outdoor conditions. H₂Bip and Bip in aqueous solutions were exposed to sunlight in La Plata city (34.90°S, 57.92°W) from Spring equinox to near Summer solstice and the spectral solar irradiance was recorded with a high-resolution spectrometer. The photochemical reactions were followed by HPLC and UV-Vis spectrophotometry. Upon sun exposure, excitation of H₂Bip leads to the formation of dimers and to its oxidation to Bip, which, in turn, is photooxidized into 6-formylpterin (Fop). Further excitation induces the oxidation of Fop to 6-carboxypterin, which is much more photostable than Bip and Fop and then it is accumulated in the solution. Rates of reactant consumption were determined under different weather conditions and the corresponding quantum yields were also calculated. We have demonstrated that solar radiation causes significant oxidation of the pterin derivatives investigated within a few minutes, even in cloudy days. Finally, the biological implications of our results are discussed.

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1. Introduction

Many living organisms are naturally exposed to sunlight. Ultraviolet (UV) solar radiation effects have been widely studied mainly because of the profound influence on human health and the effectiveness to start photochemical processes. Any increase in the UV intensity is therefore expected to produce significant changes in biological systems, which have a spectral sensitivity in this interval. The

UVA (320–400 nm) and UVB (280–320 nm) radiation can reach Earth's surface, the latter range being strongly dependent on the ozone layer depletion in the stratosphere. Human skin has a significant damage risk under UV radiation. The consequence of the radiation below 320 nm can range from a slight erythema (sunburn) to skin cancer by a long-term exposure (de Gruijl, 1999; Hermann, 1998).

Furthermore, UVA irradiation can induce modifications in DNA through photosensitized reactions (Cadet and Spaul, 2005). The melanin of the epidermis, is the main protection against the harmful effects of UV solar radiation. The vitiligo is a chronic depigmentation disorder (Glassman,

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2011), characterized by loss of melanin, where the deactivation of enzymes necessary for melanin biosynthesis takes place, causing melanin's photo-protection failure.

Pterins are heterocyclic compounds present in living systems and, depending on the oxidation state, they can be classified as: oxidized (or aromatic) and reduced pterins (Fig. 1). Dihydrobiopterin (H_2Bip) belongs to the latter group and is a naturally occurring pterin derivative involved in the metabolism of amino acids (Nichol et al., 1985). Biopterin (Bip) and other oxidized pterins, which are not present in mammals under physiological conditions, accumulate in the skin of patients suffering from vitiligo (Schallreuter et al., 2001). Among them, 6-carboxypterin (Cap), a product of Bip photolysis (Vignoni et al., 2009; Lyudnikova et al., 2009), has been isolated from the affected tissues (Rokos et al., 2002), suggesting that photooxidation of Bip takes place in vivo. Oxidized pterins are photochemically reactive upon UVA radiation exposure in aqueous solution and undergo photooxidation to produce several photoproducts and reactive oxygen species such as singlet molecular oxygen (1O_2) and hydrogen peroxide (H_2O_2) (Lorente and Thomas, 2006; Neverov et al., 1996). In addition, it has been demonstrated that Bip and its photoproducts are able to photosensitize the oxidation of biomolecules (Serrano et al., 2013; Serrano et al., 2012). Therefore, the photochemistry of pterins is of vital importance for the knowledge of the mechanism of vitiligo disease.

The photochemistry of Bip and H_2Bip upon UVA exposure has been described in detail (Fig. 1) (Vignoni et al., 2010; Vignoni et al., 2009; Lyudnikova et al., 2009). Briefly, UVA excitation of H_2Bip in the presence of O_2 leads to two photochemical pathways: the formation of isomeric dimers with molecular masses equal to exactly twice the molecular mass of the reactant and the oxidation to its aromatic analogue, Bip. This latter reaction has been considered as a potential source of Bip in the skin (Vignoni et al., 2010). This compound, under aerobic conditions, is photochemically converted into 6-formylpterin (Fop), which, in turn,

undergoes photooxidation to Cap, which is much more photostable than Bip and Fop. However, those studies have been performed using quasi-monochromatic sources under controlled laboratory conditions.

On the other hand, the effect of sunlight on Bip and H_2Bip has not been investigated. The aim of this work is to find out if the energy of the sun under different conditions is enough to cause significant chemical changes in Bip and H_2Bip and to compare those reactions triggered by sunlight to the photochemistry of these compounds already described in the literature. Therefore a study under outdoor conditions was performed to characterize the photochemical behavior of H_2Bip and Bip in a natural environmental context. In particular, we have identified the photoproducts, analyzed the kinetics and determined the quantum yields, simultaneously with the measurement of solar energy and the determination of atmospheric variables. The results are analyzed in the context of the general photochemical behavior of pterins in aqueous solution and the biological implications are discussed.

2. Materials and methods

2.1. General

H_2Bip , Bip and other pterins were purchased from Schircks Laboratories (Switzerland) and used without further purification. Other chemicals were from Sigma Chemical Co. The pH of the aqueous solutions was adjusted by adding drops of HCl or NaOH solutions from a micropipette. The concentrations of the acid and base used for this purpose ranged from 0.1 to 2 M. The ionic strength was approximately 10^{-3} M in all the experiments. As a control, the electronic absorption spectrum of each solution was recorded on a Shimadzu UV-1800 spectrophotometer.

2.2. Solar spectral irradiance measurements

Irradiance (E) is defined as the radiant power incident on a small element of surface containing the point under consideration divided by the area of the element. Spectral irradiance (E_λ) is the derivative from E with respect to wavelength (λ) and is expressed in $W m^{-2} nm^{-1}$. The photon irradiance ($E_{n,p}$) is the number of *einstein* (mol of photons) per time interval (photon flux, $q_{n,p}$), incident on a small element of surface containing the point under consideration divided by the area of the element (Braslavsky, 2007). Spectral photon irradiance ($E_{n,p,\lambda}$) is the derivative from ($E_{n,p}$) with respect to λ and is expressed in $einstein m^{-2} s^{-1} nm^{-1}$. E_λ can be converted into $E_{n,p,\lambda}$ by means of the Planck relation:

$$E_{n,p,\lambda} = E_\lambda \cdot \left(\frac{\lambda}{N_A \cdot hc} \right) \quad (1)$$

where N_A is the Avogadro constant, h is the Planck constant and c is the speed of light.

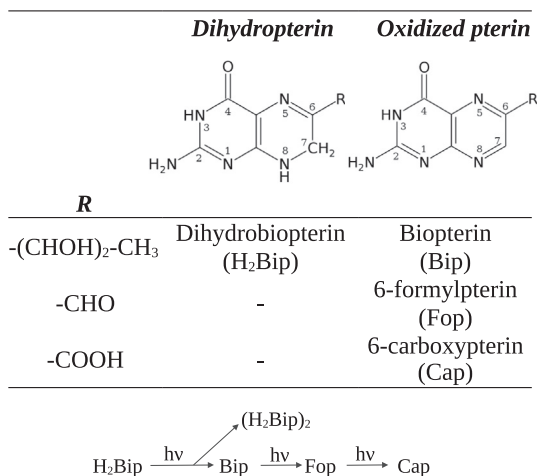


Fig. 1. Chemical structures of the pterin derivatives studied in this work and photochemical reaction pathway.

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