Structural and optical properties of Heraclenin; A bio-organic molecule from Prangos Pabularia

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By column chromatography technique, heraclenin, a linear furano-coumarin with molecular formula C16H14O5, was isolated from the root parts of the plant Prangos pabularia. Various techniques, like X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), optical microscopy (OM), UV–Visible spectroscopy and photoluminescence (PL) were used to study structural and optical properties of the isolated compound. The XRD analysis of the compound predicts its structure to be orthorhombic. The melting point of the compound was found to be 112–114 °C. From SEM and optical images, the compound was found to be comprising of large micro crystals and these exhibit irregular surface morphologies. UV–vis spectral studies predicted low absorbance by the compound in the entire visible range. The compound exhibited indirect allowed and forbidden indirect allowed transitions with optical band gap (Eg) around 3.67 eV and 3.91 eV. PL studies showed good emission in visible region at certain wavelengths. These properties of the compound can be exploited for its application in optoelectronics.

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1. Introduction

The rapid development of organic electronics has been as a result of a wide attention of researchers towards the organic semiconductors because of their significant physical and chemical properties [1–10]. The application of organic semiconductors in flexible electronics is due to their promising mechanical and thermal properties. The incorporation of functionalities through atomic or molecular design in organic semiconductors is possible because of their chemical stability and solubility. The best known organic compounds containing polycyclic aromatic hydrocarbon skeleton are suitable for possible applications in Organic-Light-Emitting Diodes (OLEDs) [11–14]. The mostly used efficient electron/hole-transporting materials or host emitting materials in OLED applications in recent times include naphthalene, anthracene, perylene, fluorene, carbazole, pyrene and their derivatives. As per literature, the pyrene based, multiple conjugated, fluorescent light-emitting materials have been synthesized and their photophysical properties have been well studied [11]. There are reports of successful application of pyrenes as efficient hole/electron-transporting materials or host emitters or emitters in OLEDs [1]. Preparation of pyrene-based, cruciform-shaped π-conjugated and blue-light-emitting architectures with an emphasis on synthetic design, that promise their potential applications in OLEDs, can be achieved [1,11].

The asymmetric polarisability of the organic materials is enhanced by increase in nonlinearity due to the delocalized π-electron system between donor and acceptor groups [9–11]. We report the structural and optical properties of heraclenin, a furano coumarin, isolated from the ethyl acetate extract of the root parts of the plant Prangos pabularia in present article, in continuation to our previous studies on coumarins [15,16].

2. Experimental

Heraclenin, molecular formula C16H14O5, molecular mass 286, melting point 112–114 °C was isolated from ethyl acetate extract of the root parts of the plant P. pabularia by column chromatography using silica gel as adsorbent. The structure of the compound was elucidated by extensive spectral analysis [1H-NMR, 13C-NMR, UV, IR and MS] and comparison of the data values with the values reported in literature [17,18]. Melting point (m.p) was determined in centigrade scale in one end open capillary on Buchi 570 melting point apparatus. The 1H and 13C NMR spectra were recorded by Bruker 500 (125 MHz) instrument using TMS as internal standard and CDCl3 as solvent. The UV spectra were recorded on a Shimadzu
UV–1601 spectrometer using dichloromethane as solvent. The Column chromatography was carried out with Merck silica gel (60–120 mesh and 100–200 mesh). Aluminium sheets, precoated with silica gel 60 F254 (20 × 20 cm, 0.2 mm thick; E-Merck) were used for TLC to check the purity of the compound and visualized under UV light (254 and 366 nm) followed by ceric sulfate as spraying reagent. The crystalline structure of this compound was analyzed by a Rigaku powder x-ray diffractometer with Cu Kα radiation with wavelength is 1.540598 Å and a graphite mono-chromator. Optical images were taken by Trinocular Microscope (LIECA DM LS2). SEM images were carried out using Environmental Scanning Electron Microscope (ESEM) by FIB Netherlands. Photoluminescence (PL) experiment was carried out using Perkin-Elmer LS-55 spectrometer using dichloromethane as solvent, at room temperature with an excitation of 260 nm He–Cd laser. PL spectrum of the sample was detected with a grating monochromator and a standard CCD detection system.

3. Results and discussions

3.1. Structural analysis

The structure of heraclenin (inset Fig. 1) was elucidated on the basis of spectral analysis (MS, IR, UV and NMR). The crystallinity of heraclenin is quite clear from the observed XRD pattern as depicted in Fig. 1. The sharp peaks of the sample occur at specific Bragg’s angles. The obtained diffraction pattern of the present sample was indexed using Powder-X software. On the basis of cell parameters the structure of heraclenin was found to be orthorhombic with four molecules per unit cell and the lattice parameters a = 14.44393 Å, b = 7.182035 Å, and c = 26.94950 Å, α = β = γ = 90.00°. The data values are in agreement with similar systems reported in literature [19–21].

The SEM image of heraclenin is shown in Fig. 2 a. As per the study, the micro crystals have grown with irregular morphology. In addition, these crystals showed a sluggish or blurred quality and were whitish brown in color without having significant transparency. The possible reason behind this observation may be the nucleation centers and the ordering of carbon molecules [22], since these micro crystals are obtained by high evaporation rate at low temperature, leading to irregular morphology with dislocation/defect centre [23]. Fig. 2b shows the optical image of heraclenin (10× magnification), which inferred that the compound consists of micro crystals with different sizes and morphologies.

The FTIR spectrum of heraclenin is shown in Fig. 3. The compound showed various characteristic bands with varying intensities. The band with strong intensity at around 1722 cm⁻¹ is due to α-unsaturated-δ-lactone. The bands at around 1598 and 1491 cm⁻¹ are due to the presence of aromatic moiety and bands at 1383, 1386 cm⁻¹ are because of gemdimethyl [17,18]. The band at 2970 cm⁻¹ was assigned to an asymmetric C–H stretching of methyl groups and another at 2852 cm⁻¹ was assigned to its symmetric one. The compound also showed bands at 1465 cm⁻¹ and 1380 cm⁻¹ due to asymmetric and symmetric bending vibration of methyl groups respectively. The peak at 3435 cm⁻¹ was assigned to C–C–O’ symmetric stretching and 3133 cm⁻¹ to aromatic C–H stretching. The compound displayed a peak at around 1155 cm⁻¹ due to C–O stretching vibrations.

![Figure 1](image1.png)  
**Fig. 1.** XRD pattern Heraclenin. Inset shows its molecular structure.

![Figure 2](image2.png)  
**Fig. 2.** a. SEM micrograph of Heraclenin. b Optical image of Heraclenin.

![Figure 3](image3.png)  
**Fig. 3.** FT-IR spectrum of Heraclenin.
3.2. Optical properties

Heraclenin exhibited less absorbance in the wavelength range 400–700 nm as is evident from its UV–visible spectrum (Fig. 4). The absorbance due to electronic transitions in this region is also absent and the possibility of any overtones or combination modes above the threshold values of wavelength is not clearly seen. Since, less absorbance in the entire visible region is an essential condition for the Non-linear optical (NLO) applications [24,25], high transmittance shown by these crystals projects them as possible future candidate for the generation of second harmonic light (532 nm) as well as third harmonic generation (354.6 nm) for Nd:YAG laser (1064 nm).

In most semiconductors, the fundamental absorption edge follows the exponential law. The absorption coefficient for the semiconductors above the exponential tail, was seen to obey the equation [26],

\[ \alpha h\nu = A(h\nu - E_g)^n \]

where \( \alpha \) is the absorption coefficient, \( \nu \) is angular frequency, \( A \) is a constant and \( n \) is an index the values of which, depending on the nature of electronic transition responsible for the absorption can be 1/2, 3/2, 2 and 3. For the direct allowed transition, \( n = 1/2 \), for forbidden direct transition, \( n = 3/2 \), for the indirect allowed transition, \( n = 2 \) and for forbidden indirect transition, \( n = 3 \) and \( E_g \) is the optical band gap. Optical absorption coefficient \( \alpha(\nu) \) has been obtained and the results may be displayed in a number of ways as a function of photon energy (h\( \nu \)).

By plotting \( (\alpha h\nu)^n \) as a function of \( h\nu \), taking \( n \) as 1/2, 2, 3 and 3/2 respectively, the band gap can be studied. Here in our case, only linear fit between \( (\alpha h\nu)^n \) as a function of \( h\nu \) plot (Inset Fig. 4) was obtained for \( n = 1/2 \) and 3, respectively, showing that the compound has only indirect allowed and forbidden indirect allowed transitions. The optical band gaps (\( E_g \)) of 3.67 eV (for \( n = 0.5 \)) and 3.91 eV (\( n = 2 \)) were obtained for these transitions, respectively.

The absorption coefficient \( \alpha \) characterizes a spectral change in the optical absorption near the band edge which increases exponentially with \( h\nu \) obeying the exponential relation [27]:

\[ \alpha = \alpha_0(h\nu/E_g) \]

where \( \alpha_0 \) is constant and \( E_g \) is interpreted as the width of the localized states in the band gap (it actually gives the degree of disorder). By plotting \( \ln(\alpha) \) as a function of \( h\nu \), one can calculate \( E_g \). Here, we have calculated \( E_g \) as 0.112 eV (plot not shown here).

The optical properties of these crystals mentioned above can briefly be explained as: when a molecule or compound absorbs light of an appropriate wavelength, an electron is excited to a higher energy level. Also, ultraviolet (UV) and visible (Vis) light has enough energy to cause electronic transitions. The higher energy electronic transition is promotion of an electron from a \( \pi \) bonding molecular orbital into a \( \pi^* \) antibonding molecular orbital, known as \( \pi-\pi^* \) transition (ligand \( \pi-\pi^* \) transition). This means that only compounds with \( \pi \) electron and non-bonding electrons can produce UV–Vis spectra [9–11].

The observed low absorbance/high transmittance in heraclenin in the entire visible region are due to \( \pi-\pi^* \) transition. Thus, the crystals can be useful in NLO devices as the transmittance in visible region is much higher than that of various other organic molecules.

The photoluminescence (PL) spectrum of the heraclenin (Fig. 5) after excitation with 260 nm at room temperature in range of 375–665 nm, shows various intensity peaks, the dominant ones being at 404 nm (violet), 430 nm (indigo) and 455 nm (blue), possibly due to \( \pi-\pi^* \) transition of this molecule predicting that the compound can be used for organic optoelectronic devices with or without any modifications.

Most of the organic crystals behave as NLO material due to the \( \pi \) bonding [28]. The absorption at various bands suggests that there can be emission of different radiations using appropriate laser, and can lead to second harmonic generation [21]. This also supports the possible usefulness of the present compound as NLO material. Further studies to establish the nonlinear optical properties of the system are in progress.

4. Conclusion

Heraclenin was isolated from the root parts of the plant \( P.\ \text{pabularia} \) by using column chromatography. The compound was characterized by various techniques: XRD, SEM, OM, FT-IR spectroscopy, UV–Vis spectroscopy and PL spectroscopy. The compound showed orthorhombic structure with wide optical band gap and high transmittance in the entire visible region. In addition, on excitation by 260 nm light source, the compound showed various emission bands. The observed optical properties exhibited by the under study compound predict its bright future in modern organic electronics.

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References

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