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## Research Article

# EXPERIMENTAL SPECTROSCOPIC (FT-IR, NMR, UV-VIS) AND DFT STUDIES OF 7-HYDROXY-6-METHOXY COUMARIN

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### ABSTRACT

The vibrational fundamental modes of 7-Hydroxy-6-methoxy coumarin (Scopoletin) have been analyzed by combining FTIR, NMR, UV-Vis and quantum chemical calculations. The structural parameters of the compound are determined from the optimized geometry by B3LYP method with 6-311++G(d,p) basis set. The harmonic vibrational frequencies were calculated and have been compared with experimental FTIR spectra. <sup>1</sup>H and <sup>13</sup>C NMR spectra have been analyzed and <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) chemical shifts are calculating using gauge independent atomic orbital method (GIAO). The theoretical UV-Vis spectrum of the compound and the electronic properties, such as excitation energies, oscillator strength, wavelength, HOMO and LUMO energies were calculated by time-dependent density functional theory approach (TD-DFT). Thermodynamic properties like heat capacity, entropy and enthalpy have been calculated for the molecule at different temperature.

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## INTRODUCTION

Coumarins are naturally occurring heterocycles which has been previously isolated from the plant species such as *Scopolia japonica*, *Gelsemium sempervirens*<sup>1</sup>, *Malvasilvestris*, *Anthocephalus chinensis*<sup>2</sup>, *Morindacitrifolia*, *Bombax Ceiva*, *Tiliacordata* etc., and also from the shoot culture of *Ruta graveolens*<sup>3</sup>. Coumarin scaffolds possess a wide spectrum of biological activities, very particularly anti-spermatogenic, anti anti-tumoural, anti-HIV and anti-tubercular agents. coumarins have been also found to possess choleric, analgesic, anti-spermatogenic, anti-oncogenic<sup>1</sup> and diuretic properties. Coumarins are also used as a fluorescent label in different chromatographic techniques<sup>5</sup> and in fluometric analysis<sup>6</sup>. Coumarins have an inherent understanding of biology space, and their synthetic derivatives have played a significant role in the discovery and development of drugs. Owing to the importance listed above coumarin scaffolds are of prime interest to the researchers in the area of drug design and discovery.

### Experimental Method

The compound 7-Hydroxy-6-methoxy coumarin (Scopoletin) was isolated as white needle crystals, m.p. 205-207°C, from the plant extract of *Anthocephalus chinensis* with a stated purity of greater than 98% with the help of high performance liquid chromatography and it was used as such without further purification. Scopoletin has also been named as gelseminic acid, chrysotropic acid and β-methylaesculetin<sup>4</sup>. The structure of 7-Hydroxy-6-methoxy coumarin compound is shown in Fig.1. The Fourier Transform Infrared spectra were recorded in the range 4000-400 cm<sup>-1</sup> using a Thermo Nicolet Avatar, 370 FT-IR spectrometer. The sample was prepared in the form of a pellet by mixing KBr and 7-Hydroxy-6-methoxy coumarin. The UV absorption spectra of 7-Hydroxy-6-methoxy coumarin were examined in the range 200-500nm using the Shimadzu 1800, UV-vis recording spectrometer. The UV pattern is taken from a 10<sup>-5</sup> M solution of 7-Hydroxy-6-methoxy coumarin, dissolved in methanol. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were

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recorded on a Bruker DRX-300 spectrometer operating at 300MHz. The measurements were done in dimethyl sulphoxide (DMSO) solution. The solution was prepared by dissolving about 2mg of the sample in 0.6mL of DMSO. The spectra have following experimental parameters: number of scans 32; spectral width 9615.385 Hz; acquisition time 3.40 s. Chemical shifts were reported in ppm relative to TMS.

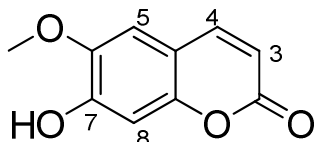


Fig 1 Structure of compound 7-Hydroxy-6-methoxy coumarin

### Computational Details

The entire calculations were performed using the Gaussian 09W program package, invoking gradient geometry optimization. The initial geometry was generated from standard geometrical parameters and was minimized without any constraint in the potential energy surface at the B3LYP level, adopting the standard 6-311++G(d,p) basis set. The optimized structural parameters were used in the vibrational frequency calculations to characterize stationary points as minima. We have utilized the density functional theory (DFT) with the three-parameter hybrid fundamental (B3LP) for the exchange part, and the Lee-Yang-Parr (LYP) correlation function for the computation of the molecular structure, vibrational frequencies and energies of the optimized structure. Finally, the calculated normal mode vibrational frequencies also provided the thermodynamic properties through the principles of statistical mechanics. Electronic transitions and oscillator strengths for 7-Hydroxy-6-methoxy coumarin was calculated by TD-DFT using 6-311++G(d,p) basis set and B3LYP functional after taking into account configuration interaction between singly excited states. All molecular geometries were visualized using Chemcraft and Gauss-View program. The proton and carbon NMR chemical shifts were calculated with gauge including atomic orbital (GIAO) approach by applying B3LYP/6-311++G (d,p) method of the title molecule and compared with the experimental NMR spectra.

## RESULTS AND DISCUSSION

The optimized structure of 7-Hydroxy-6-methoxy coumarin with numbering scheme for the atoms is presented in Fig.2 and it belongs to  $C_1$  point group symmetry.

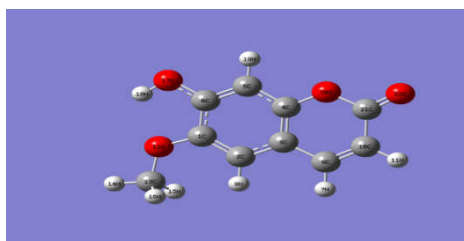


Figure 2 Molecular Structure of 7-Hydroxy-6-methoxy coumarin with atom numbering scheme.

The optimized structural parameters like bond length, bond angle and the dihedral angle of 7-Hydroxy-6-methoxy coumarin determined by B3LYP method with 6-311++G(d,p) basis sets are summarized in the Table 1. All the C-H bond length of Scopoletin averages to 1.08 $\text{\AA}$  except methoxy group.

The ring C-O bond length is usually 1.43 $\text{\AA}$ , but a reduction in bond length (C1-O2, C4-O20, C6-O17 = 1.35 $\text{\AA}$ ) observed in the present investigation is due to the fusion of benzene ring with the  $\alpha$ -pyrone ring through O20 atom. The substituent plays a vital role on the structural and electronic properties of the molecules. The methoxy group substitution effect the regular hexagonal structure of their respective rings, which is evident from the observed bond angles. The decrease in bond angles C6-C1-O12 (113.98 $^\circ$ ) in turn reduces the C1-O12 bond length (1.35  $\text{\AA}$ ).

### Vibrational Analysis

The observed FT-IR spectra of titled molecule were made with the help of Gauss-View program. The C=O stretching band is characterized by a very strong and sharp band appearing approximately at 1700  $\text{cm}^{-1}$ . So for the compound Scopoletin the C(21) = O(22) stretching vibration is allotted for the simulated value 1720  $\text{cm}^{-1}$  and its experimental counterpart in IR spectrum exactly coincide with this value. The two ring CO stretching vibrations (C4-O20 and C21-O22) are predicted at 851 and 983  $\text{cm}^{-1}$ . Both of these vibrations are found in IR at 865 and 990  $\text{cm}^{-1}$ , respectively. The methoxy group C-O stretching vibrations are calculated at 1024 and 1037  $\text{cm}^{-1}$ .

### NMR Analysis

The chemical shifts of the compounds are reported in ppm relative to TMS for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra and are listed in Table. In the  $^1\text{H}$  spectrum of Scopoletin, two singlet chemical shifts for aromatic hydrogen at 7.20 (1H, s) and 6.77 (1H, s) ppm are observed and two doublet chemical shift at 6.19 (1H, d,  $J=9.6$ ) and 7.80 (1H, d,  $J=9.6$ ) ppm is observed for pyron ring. By contrast electron donating atom or group increases the shielding and moves the resonance towards to a lower frequency. Accordingly for 7-Hydroxy-6-methoxy coumarin the chemical shift value of -OCH<sub>3</sub> attached H atom experiences a lesser value at 3.78 (3H, s) ppm and fairly agrees with the calculated value. Data shows good agreement between experimental and calculated chemical shifts.

Table 1 Experimental and Theoretical isotropic chemical shifts with respect to TMS for 7-hydroxy 4-methoxy coumarin

Atom Position	Chemical shift (ppm)	
	Exiperi-mental	Calculated
C-1	151.1	143.9
C-2	109.6	104.7
C-3	111.7	112.0
C-4	149.5	152.4
C-5	102.8	105.3
C-6	144.5	152.2
C-9	145.3	143.4
C-10	110.6	118.5
C-13	56.0	51.4
C-21	160.7	154.5
H-7	7.18	7.05
H-8	7.20	6.17
H-11	6.19	5.73
H-14	3.78	3.89
H-15,16	3.78	3.72
H-19	6.77	6.71

### UV-Visible Spectroscopy

The search of the organic materials with improved charge transfer properties requires precise quantum chemical calculations of space charge density distribution, stable and transition dipole moments, HOMO and LUMO states. The absorption in the range of UV spectrum has been taken as a

main criterion for verification of performed quantum chemical calculations. Recently it can shown that time dependent density functional theory (TD-DFT) method reproduces very accurately optical susceptibilities for a wide range of organic systems. The nature of the transition in the observed UV-Visible spectrum of the titled compound has been studied by the time dependent density functional theory. Frontier molecular orbital HOMO and LUMO determine ability of a molecular to absorb light and the molecular reactivity. The HUM-LUMO energy gap for the title compound calculated at B3LYP/6-111++G (d,p) method found to be as 4.004 eV. A combined experimental and theoretical UV-Visible spectrum analysis of the title compound indicates that the observed electronic excitation at  $\lambda_{\max} = 365$  nm corresponds to the electronic excitation calculated at  $\lambda_{\max} = 310$  nm with  $f = 0.2292$ . The difference between experimental and calculated value of band gap was due to the absorbing medium. On the basis of molecular orbital and molecular orbital coefficient analysis, nature of transition was found to be  $n \rightarrow \pi^*$

### Thermochemical Analysis

Thermochemical properties of titled molecule are dominated by molecular vibrations as electronic contribution becomes negligible due to absence of free electrons, especially at the room temperature. Various thermal parameters for titled molecule are calculated and reported in Table 2.

**Table 2** Various thermodynamic parameters for titled molecule calculated at B3LYP/6-311++G9d,p)

T (K)	H <sub>m</sub> (kcal mol <sup>-1</sup> )	C <sub>p,m</sub> (cal mol <sup>-1</sup> K <sup>-1</sup> )	S <sub>m</sub> (calmol <sup>-1</sup> K <sup>-1</sup> )
100	101.210	25.421	69.213
200	105.941	31.497	89.769
300	109.793	45.392	106.002
400	114.974	57.909	121.391
500	121.306	68.378	135.921
600	128.581	76.822	149.524
700	136.615	83.611	162.201
800	145.261	89.130	174.004
900	154.409	93.681	185.007
1000	163.472	97.480	195.289

These parameters are related to one another via standard thermodynamic relations and can be useful for the estimation of chemical reaction paths.

From table, it can be observed that these thermodynamic functions are increasing with temperature due to the fact that the molecular vibrational intensities increase with temperature. The correction equations between heat capacity (C<sub>p,m</sub>), entropy (S<sub>m</sub>), enthalpy changes (H<sub>m</sub>) and temperature (T) are fitted by quadratic formulas. The corresponding fitting equations are as follows:

$$C_{p,m} = 0.303 + 0.173T - 8 \times 10^{-5} T^2$$

$$S_m = 54.71 + 0.184 T - 4 \times 10^{-5} T^2$$

$$H_m = 98.72 + 0.025 T + 4 \times 10^{-5} T^2$$

### CONCLUSION

A systematic study has been conducted on the structural and spectral analysis of the titled molecule by spectroscopy and quantum chemical calculations. The vibrational and structural study of title compound using various spectroscopic techniques such as Ft-IR, NMR, UV-Visible and thermochemical analysis.

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