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Preparation, Full Characterization and Theoretical Studies for New Herniarin derivatives

Abstract- Novel Herniarin compounds were prepared and identified by UV-VIS, FTIR, NMR spectra. Theoretical Studies and molecular structure with optimized geometry were done by utilizing Density functional theory for the prepared compounds

Keywords- Herniarin, HOMO, LUMO, Azo dyes, DFT, Diazonium salts reaction

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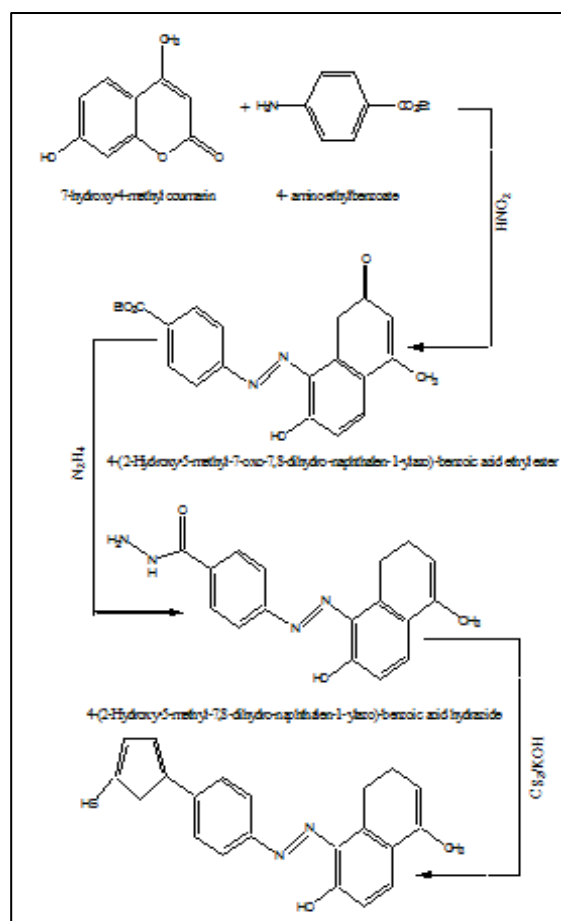
1. Introduction

Azo-dyes are the most essential and adaptable class of synthetic organic and natural compounds, with a gigantic mixture of utilizations [1]. These can be acquired effectively and cheaply utilizing a variety of diazo and coupling compound. They have high coloring and great fastness properties and wide applications in territories, for example, coloring of material strands, plastics, cowhide, paper and bio-restorative studies [2]. Coumarins assume a vital part in natural science. While coumarin is a colorless compound, some of its derivatives shading and extreme fluorescence [3]. The preparation of coumarin dyes have pulled in the consideration of scientific experts for a long time, as countless items contain this heterocyclic core. These colors are likewise abused in concoction, biochemical, physical and pharmaceutical applications. The coumarin is not fluorescent, but rather the presentation of an electron-pulling back gathering, for example, a diazotized fragrant amine or an acetyl gathering makes it very fluorescent. The coumarins are for the most part exceptionally helpful mixes for concoction change because of the simplicity of blend [4]. Azocoumarin colors were combined in two-stage system, arrangement of diazonium salt, then coupling response with coumarin [5].

2. Results and Discussion

For the preparation of target compound namely 7-hydroxy-4-methyl-8-((E)-[4-(5-sulfanyl-1,3,4-oxadiazol-2-yl) phenyl] diazenyl)-2H-chromen-2-one, the reaction scheme was outlined above in Scheme 1, and it start from herniarine, that can be synthesized by the refluxing of resorcinol and ethyl acetoacetate with concentrated sulphuric acid. As described in the literature [6,7], the Pechmann reaction was carried out with toluene as a solvent. The FTIR spectra of target compounds

demonstrated absorption bands in the 1966 cm^{-1} ($\text{C}=\text{O}$), 1614 cm^{-1} ($\text{C}=\text{N}$ of oxadiazole), and 1138 cm^{-1} (C-O-C cyclic group in oxadiazole), and 1512 cm^{-1} (N=N stretching), and 1336 cm^{-1} (C=S), and 1566 cm^{-1} (C=C). The ^1H NMR spectra (300MHz in 6-d-dimethylsulfoxied) 10.23 δ (s,1H,OH), 2.280 δ (s,3H,CH₃), 5.845(s,1H,C=C-H),6.447(s, 1H) 7.283-7.311(d,1H), 6.454-6.565(d,1H)12.09(s, 1H,SH)ppm.



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Scheme 1: Reaction sequences of the synthesis of 7-hydroxy-4-methyl-8-{{(E)-[4-(5-sulfanyl-1, 3, 4-oxadiazol-2-yl) phenyl] diazenyl}-2H-chromen-2-one

I. Computational Studies

1. Mulliken Charges and Stabilities

The hypothetical studies [8-10] for new herniarin uncovered that the nuclear charges have been influenced by the ring's vicinity substituent. Molecular geometries of the all molecules were fully optimized by DFT (density functional theory) B3LYP method [11] utilizing 3-21G basis set [12] by ChemBioOffice 2010 software used for all geometry optimizations is appeared in Figure 1, where the ascertained nuclear charge for the novel herniarin is likewise shown, Table 1. Highest atomic charge is at [O (10) -0.7414] and the next values were at [O (12) -0.7217] and [O (11) -0.6327]. These outcomes plainly showed that these three molecules are the most responsive destinations toward the responses and holding with the metal. The ascertained bond and wind edges and three-dimensional structure, demonstrated that

the molecule wasn't planar additionally the stereochemistry is N (10)-C (26): (E), N (11)-N (12): (Z) and C (15)-C (14): (Z). The C (30)-C (31) bond length is 1.3941; N (10)-C (26) is 1.2983 and C (1)-O (8) is 1.2210.

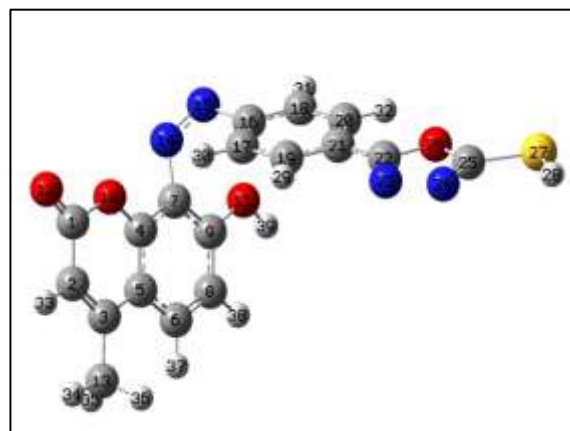


Figure 1: 3D-geometrical structures for new herniarin

Table 1: The Mulliken; Charges; of; new synthesized; herniarin; derivative

Atom	Mulliken	Atom	Mulliken	Atom	Mulliken
C1	1.156964	N14	-0.052995	S27	-0.106046
C2	-0.408593	N15	-0.136177	H28	0.069902
C3	0.486096	C16	0.172813	H29	0.090956
C4	0.475107	C17	-0.139398	H30	0.084628
C5	-0.370339	C18	-0.046103	H31	0.078255
C6	0.132325	C19	-0.008443	H32	0.077890
C7	-0.080630	C20	-0.027469	H33	0.063015
C8	-0.216405	C21	-0.085766	H34	0.021037
C9	0.445643	C22	0.537280	H35	0.025003
O10	-0.741419	N23	-0.245402	H36	0.020916
O11	-0.632710	N24	-0.386466	H37	0.062283
O12	-0.717371	C25	0.586957	H38	0.037707
C13	-0.037652	O26	-0.488520	H39	0.303127

2. Density Function Theory (DFT)

DFT was done for the new herniarins. The advanced atomic structures of the stable structures are appeared in the Figure 1. Sub-atomic the orbital counts give a point-by-point depiction of orbitals containing spatial qualities, nodal examples and individual molecule commitments [13]. The form plots of the boondocks orbitals for the ground condition of new herniarins were appeared in Figure 2, including HOMO and LUMO [14]. It could be shown from Figure 2 that the HOMO orbitals are situated on the substituted particle while LUMO orbitals look like those got for the un-substituted atom and along these lines;

the substitution has an impact on the electron gift capacity, yet just a little effect on electron acknowledgment capacity [15]. The orbital vitality levels of HOMO and LUMO of new herniarin are - 6.0012 and - 2.3360 eV separately, and the heat of formation is 31.896 Kcal/Mol. It can be seen that the vitality crevices in the middle of HOMO and LUMO speaks the truth 3.6649 (eV.) for new herniarin, and the lower quality in the HOMO and LUMO vitality hole clarify the possible charge exchange cooperation occurring inside of the molecules[16].Figure 2. HOMO and LUMO energies of new herniarin.

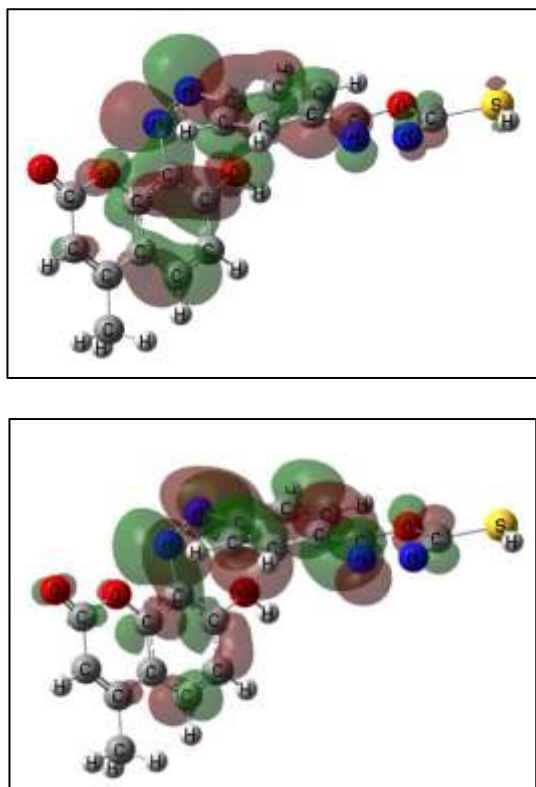


Figure 2: HOMO and LUMO energies of new herniarin

3. Experimental Section

I. General

The chemicals that utilized in our preparation were supplied from Fluka and Sigma-Aldrich, and the purity was done by thin-layer-chromatography and the spot was appeared in 365 nm UV light. Infrared-spectrum was recorded utilizing SHIMADZU FT-IR 8400S spectrophotometer, at the Chemistry Department, Al-Mustansyriyah University. NMR spectrum with the DMSO-d₆ as a solvent was done on Bruker-DMX 500-spectrophotometer-300MHz-spectrometer at department of chemistry, Al-Bayt University, Jordan. Melting point was recorded on Gallenkamp-M.F.-B00.010- F.

II. Synthesis of 7-hydroxy-4-methylcoumarin

A mixture of the resorcinol (30 mmol), ethyl acetoacetate (30 mmol) and sulfuric acid was heated at 100-120 °C for 3 hrs. Poured the mixture (that cooled to room temperature), into 50 g of crushed-ice. Formed crystals were filtered off and suspend in water for washing than dried. Recrystallized from the ethanol to give 7-hydroxy-4-methylcoumarin.

III. Synthesis of ethyl 4-[(E)-(4-methyl-7-hydroxy-2-oxo-2H-chromen-8-yl) diazenyl] benzoate

- ϵ aminobenzoic acid ethyl ester (0.01 moles) was added to conc. HCl (2.25 ml) with H₂O 4 mL. Stirred the solution for ten minutes before being

cold at (0-5) C°. Sodium nitrite (0.011 moles, 0.76 gm) in water (2.5 ml) was added drop-wise than stirred for 10 minutes and the resulting solution of diazonium salt was added drop wise to mixture of 7-hydroxy-4-methylcoumarin (1.7620g, 0.01 mole) in ethanol and 10% NaOH (10 ml) at (0C° -5C°) and pH=5.5. After completion of the addition, stirred the mixture for addition 20min. than was leave it for addition one hour. Filter the solid and wash with distilled water. Recrystallization from ethanol after dried.

VI. Synthesis of 4-[(E)-(4-methyl-7-hydroxy-2-oxo-2H-chromen-8-yl) diazenyl] benzohydrazide

To a solution of ethyl 4-[(E)-(4-methyl-7-hydroxy-oxo-2H-chromen-8-yl) diazenyl] benzoate(0.06 mole, 9.9114 g) in (25ml) of ethanol, hydrazine hydrate (80%) (moles, 30 ml) was added drop wise with stirring. Refluxed for (12 hour), cooled. After the formation of the solid, filtration and recrystallization were need by using of ethanol and water with the percentage (1:1).

VII. Synthesis of 4-methyl-8-7-hydroxy-{(E)-[4-(5-sulfanyl-1,3,4-oxadiazol-2-yl) phenyl] diazenyl}-2 H- chromen-2- one

To a mixture of compound 4-[4-methyl-7-hydroxy-2-oxo-2H-chromen-8-yl) diazenyl] benzohydrazide (0.01 mole, 3.54 g.) in a solution of potassium hydroxide (0.01 mole, 0.56 g.), (100 ml) of ethanol (96 %) was added. To the above solution, carbon disulfide (0.2 mole, 12 ml) was added slowly with stirring. The mixture was refluxed for (5-6 hrs.) until the liberation of dihydrogen sulfide (H₂S) gas was ceased. After that, the mixture was cooled and concentrated under vacuum, then poured slowly with stirring in ice path, than acidified by diluted HCl to adjust the pH at 5.5. Resulting crude was recrystallized from acetone.

4. Conclusions

In this study, the new herniarin derivative had been prepared and the structures were elucidated utilizing different techniques. These compounds were theoretically studied using utilizing and the charges of atoms in addition to stereo-chemistry were calculated and found not-planar.

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Author(s) biography



Dr. Khalida F. AL-Azawi was born in Baghdad, Iraq in February 1976. She received her B.Sc. and M.Sc. degrees in 2000 and 2003 respectively from University of Baghdad, Iraq. In 2013, she received his PhD degree from University of Baghdad, Iraq. Since 2006; she has been a Lecturer at the University of Technology, Iraq. The field of interest, Organic Chemistry, Synthesis of Organic Compounds, Theoretical Studies of Organic Compounds *and* Identification of Organic Compounds.