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Anti-UV Activity and Electronic Transition Study of 1,3-Diphenyl-2-Propenone Using Semi-Empirical Method ZINDO/s

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Anti-UV activity of 1,3-diphenyl-2-propenone (chalcone) has been determined by UV-visible spectrophotometry. A study of the electronic transition of this compound was performed using semi-empirical ZINDO/s calculations. The results of the anti-UV activity of 1,3-diphenyl-2-propenone was measured with the highest sun protection factor (SPF) value of 5.592. The lowest percentage of erythema transmission (%Te) is measured at 0.62 %, while the percentage of pigmentation transmission (% Tp) is lowest at 20 % at 10 ppm concentration. Electronic transition observed 4 peaks of UV spectrum result of semi-empirical modeling of ZINDO/s with molecular orbital transition π to π* at wavelength 188.94, 211.42 and 242.60 nm. While the molecular orbital transition n to π* occurs at a wavelength of 280 nm.

Keywords: Anti-UV, ZINDO/s, 1,3-Diphenyl-2-propenone, Sun protection factor.

INTRODUCTION

Sunscreen is an active ingredient capable of absorbing, reflecting, or dissipating UV radiation at a wavelength of 290-400 nm. Sunscreen cream can absorb at least 85 % of sunlight at a wavelength of 290-320 nm [1]. Exposure to excessive sunlight can cause skin wrinkles, black spots, premature aging to cause skin cancer. Ultraviolet rays can be divided into UV-A with wavelengths of 320-400 nm and UV-B rays with wavelengths 280-320 nm and UV-C rays of 100-280 nm length [2]. UV-A rays have less energy than UV-B and UV-C, but have a greater light identity up to the surface of the earth, causing skin discolouration to reddish brown. UV-B rays have greater energy than UV-A but fewer light intensities reach the surface of the earth so that less effect on the body. While UV-C rays are the highest and most dangerous UV rays among other UV rays but will naturally be absorbed by the ozone layer in atmospheres [3]. One way that is done to overcome this is with the use of sunscreen cream.

Sunscreen is a compound that can be used to protect the skin from sunburn, especially ultra violet (UV). To protect the skin from UV radiation, it is made cosmetic sunscreen that can absorb ultraviolet rays from sunlight effectively. Sunscreen material can be obtained synthetically or naturally. Synthetic sunscreen materials are often used in sunscreen preparations as physical and chemical absorber. For UV blockers physically commonly used TiO_2 and ZnO to block UVB/UVA [4]. The use of TiO_2 in the manufacturing of sunscreen because it has physical properties that have high refractive index and high UV absorption. TiO_2 and ZnO are the chemical compounds that have mild skin irritation rates compared to other chemical compounds.

Several agents are beginning to emerge by exploiting chemical molecules of UV radiation that are synthesized in a very long process and relatively expensive materials specifically to absorb or bend UV light as a formulation of sunscreen products [5]. Several classes of active compounds such as flavanoid, tannin, anthraquinone, cinnamon, xanton and other secondary metabolites, have been tested to be used to absorb UV light [6]. One of the compounds derived flavonoids that can probably absorb UV radiation is a chalcone. The chalcone compound has the formula $C_{15}H_{12}O$ molecule with the name of 1,3-diphenyl-2-propene-1-one (1,3-diphenylpropenone) slightly soluble in ether, chloroform, carbon disulfite, benzene and slowly soluble in alcohol. This compound includes a compound having a high boiling point of 354-348 °C, a melting point of 52-53 °C and having a refractive index of 1.6458. The 1,3-diphenyl-2-propenone has 2 aromatic rings connected by α and β-unsaturated ketones [7]. Characteristics of molecules of 1,3-diphenyl-2-propenone which have chromophore groups, can be measured and theoretical studies using computational modeling on the transition of the electronic band of the compound [8].

The modeling of salicylic acid compounds as UV absorbing compounds has been done by using the semi-empirical method of ZINDO/s, by studying the electronic transition spectra [9]. The ZINDO/s method is also used in the theoretical study of organic compounds in excited states involved in the HOMO-LUMO transition [10]. The semi-empirical method of ZINDO/s is widely used to describe electronic structures and spectral features in organic compounds especially coloured compounds [11]. The superiority of the ZINDO/s method of other semi-emprical methods is its ability in electronic spectroscopy analysis in UV-visible, IR and NMR [12]. Using the semi-empirical method of ZINDO/s, the theoretical study of electronic transition of 1,3-diphenyl-2-propenone as an anti-UV compound was used to support the results of the spectrophotometric testing of the compound.

EXPERIMENTAL

The material used in the present study was a 1,3-diphenyl-2-propenone compound of Sigma Aldirch, ethanol p.a., from Merck, UV-visible UV-visible spectrophotometer Shimadzu UV-1800 type, Hyperchem 8.03 software.

Measurement of uptake (A) of 1,3-diphenyl-2-propenone with UV spectrophotometer: Prepare the standard solution of 1,3-diphenyl-2-propenone with 0.1, 0.5, 1, 5, 10 and 50 ppm concentration. Furthermore, standard solution measured uptake at wavelength 290-400 nm with interval 5 nm.

Determination of UV impact effectiveness (% Te), (% Tp) and SPF values: Measurement of the effectiveness of 1,3-diphenyl-2-propenone as an anti-UV-light compound was performed by determining the SPF value, percent of the transmission of eritrema (% Te) and percent of pigmentation transmission (% Tp) from spectrophotometrically obtained absorbance [13].

Percent erythema:

$$\text{Te}\,(\%) = \frac{\text{Ee}}{\Sigma\text{Fe}} = \frac{\Sigma\text{T}\times\text{Fe}}{\Sigma\text{Fe}}$$

Percent of pigmentation:

$$\text{Tp}\,(\%) = \frac{\text{Ep}}{\Sigma\text{Fp}} = \frac{\Sigma\text{T}\times\text{Fp}}{\Sigma\text{Fp}}$$

where: (% Te): value of erythema transmission, (% Tp): value of pigmentation transmission, Ee: value of erythema effectiveness, T: transmission value Fe: erythema effectiveness factor, Fp: pigmentation effectiveness factor [13].

Equation to get sunscreen value:

$$[\text{AUC}] = \frac{\text{Aa} + \text{Ab}}{2} \times \text{dPa} - \text{b}$$

where, AUC: the area under the absorption curve, Aa: absorbance at wavelength a nm, Ab: absorbance at wavelength b nm, dPa-b: wavelength difference a and b. The SPF (sun protection factor) values of each concentration were determined using the following equations:

$$\log \text{SPF} = \left(\frac{\Delta\text{AUC}}{\lambda\text{n} - \lambda\text{l}}\right)\text{fp}$$

where, λn: largest wavelength, λl: smallest wavelength, n-l: erythemogenic interval, fp: dilution factor.

Molecular structure modeling and geometry optimization: The molecular modeling of the 1,3-diphenyl-2-propenone compound was carried out using the Hyperchem 8.03 program, using the Austin model (AM1), parameterized model 3 (PM3) and modified neglect of diatomic overlap (MNDO) methods with a gradient limit of position energy change 0.001. The process is continued by geometric optimization to obtain molecular structure with minimum and stable energy.

Determination of spectrum: The structure of 1,3-diphenyl-2-propenone derived compound derived from optimization is done by single point calculation by ZINDO/s method to get electronic transition data. The difference in HOMO-LUMO orbital energy is determined by 2, with the maximum degeneration rate determined to the limit 3. The discontinuous spectra of the UV-visible wavelength area and the recording calculation are used to predict the type of activity of the anti-UV compound theoretically.

RESULTS AND DISCUSSION

Activity of anti-UV compounds: The result of the measurement of the 1,3-diphenyl-2-propenone compound by spectrophotometry shows the activity of UV-B and UV-A absorption (Figs. 1 and 2). The SPF value and percent of erythema transmission were determined from the results of UV-B absorption measurements (Table-1) with a wavelength range of 290-320 nm. While the measurement of UV-A light absorption with wavelength range 320-400 nm is used to determine percent pigmentation (Table-2).

Based on the UV-B uptake graph (Fig. 1) it can be observed that the 1,3-diphenyl-2-propenone compound has optimum uptake at a concentration of 10 ppm with an absorbance value of 0.011. The optimum wavelength tendency in the measurement of the compound from the concentration of the tested solution lies in the UV-B area at a wavelength of 300 nm. The absorbance value of the compound has a downward trend in the wavelength of the UV-A area. The area under the UV-A absorption curve [AUC] is directly proportional to the increase

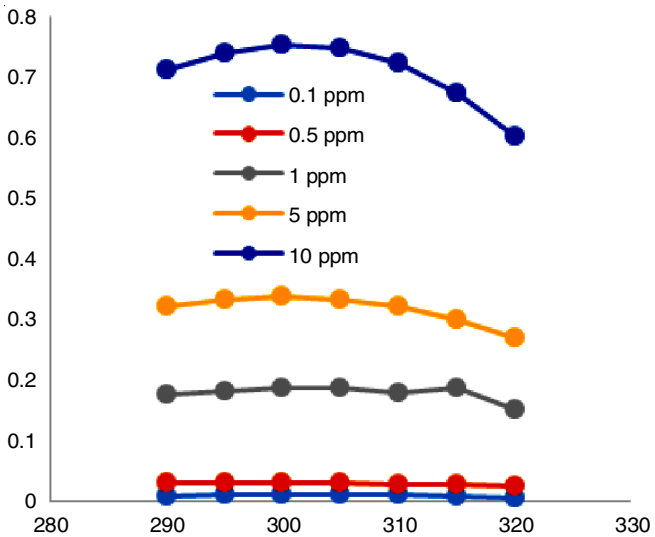

Fig. 1. Absorption graph of the 1,3-diphenyl-2-propenone in the UV-B area

TABLE-1
RESULTS OF UV-B TEST OF 1,3-DIPHENYL-2-PROPENONE

C	Absorbance							% Erythema transmission	Sun protection factor
	290	295	300	305	310	315	320		
0.1	0.008	0.01	0.011	0.011	0.009	0.007	0.006	3.07	1.195
0.5	0.029	0.03	0.03	0.029	0.028	0.027	0.025	2.94	1.071
1.0	0.175	0.182	0.187	0.186	0.179	0.186	0.151	2.08	1.544
5.0	0.322	0.333	0.339	0.334	0.321	0.300	0.268	1.51	2.157
10.0	0.712	0.741	0.755	0.748	0.724	0.675	0.603	0.62	5.592

TABLE-2
RESULTS OF UV-A TEST OF 1,3-DIPHENYL-2-PROPENONE

C	Absorbance											% Pigmentation transmission
	325	330	335	340	345	350	355	360	365	370	375	
0.1	0.005	0.003	0.002	0.001	0.002	0.001	0.001	0.001	0.002	0.001	0.001	29.39
0.5	0.021	0.016	0.012	0.009	0.007	0.007	0.006	0.004	0.004	0.004	0.004	28.87
1.0	0.128	0.101	0.076	0.056	0.038	0.026	0.018	0.014	0.013	0.012	0.010	26.26
5.0	0.226	0.179	0.134	0.095	0.064	0.045	0.033	0.025	0.020	0.016	0.013	24.26
10.0	0.508	0.402	0.301	0.211	0.141	0.096	0.067	0.051	0.040	0.031	0.026	20.00

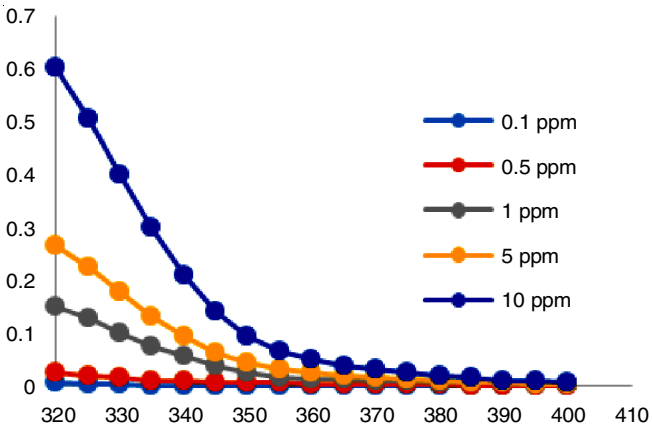

Fig. 2. Absorption graph of the 1,3-diphenyl-2-propenone in the UV-A area

in the concentration of the compound, the greater the concentration increasing the [AUC] value.

Increasing the value of 1,3-diphenyl-2-propenone concentration at UV-B wavelength measurement can decrease percent of erythema transmission (% Te) and increase SPF value (Table-1). Large percent of erythema transmission (% Te) is inversely proportional to SPF activity. The SPF values indicate the potential of 1,3-diphenyl-2-propenone in absorbing or counteracting UV-B radiation, whereas (% Te) indicates UV-B radiation that can not be inhibited by 1,3-diphenyl-2-propenone. The highest SPF value of 5.592 was shown at a concentration of 10 ppm under moderate protection category. The percentage of pigmentation transmission (% Tp) is calculated based on the magnitude of the UV-A wavelength passed. The experimental data shows, the greater the concentration 1,3-diphenyl-2-propenone impact on decreased UV-A wavelength that passed (Table-2).

Molecular modeling and geometry optimization: The study of 1,3-diphenyl-2-propenone activity against UV electromagnetic waves is done by semi-empirical computational modeling. To obtain optimal and near optimal 1,3-diphenyl-2-propenone optimization geometry is done by comparing 3 semi-empirical methods for molecular optimization. Of the three methods, among which are AM1, PM3 and MNDO, the PM3 method is obtained as a molecular optimization method that has a total molecular energy value and the smallest and nearest zero formation heat (Table-3). This method is therefore chosen as an optimization method of molecular geometry (Fig. 3).

TABLE-3
RESULTS OF GEOMETRIC OPTIMIZATION
OF 1,3-DIPHENYL-2-PROPENONE

Parameters	Energy (kcal/mol)	Heat formation (kcal/mol)
AM1	-55443.1	40.2023
PM3	-51979.1	35.3698
MNDO	-55512.1	44.2464

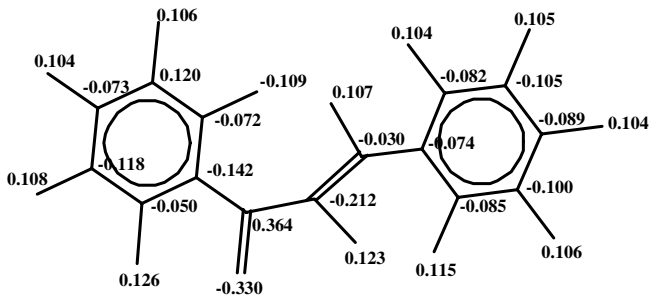

Fig. 3. 1,3-Diphenyl-2-propenone optimized by PM3

Simulation modeling of a molecular orbital transition of 1,3-diphenyl-2-propenone involving 28 atoms and 76 molecular orbitals ZINDO/s is performed under single point optimization (CI) conditions. From the simulation of electronic spectra and molecular orbital indicates the activity of UV light absorption. The transition of the molecular orbitals is shown in the π orbitals shown with the electronic peak peaks of 188.94, 211.42, 242.60 and 280 nm (Table-4). With relatively small intensity, some peaks of electromagnetic spectra may be unreadable on the experimental results. The ZINDO/s spectral peak represents the electronic transition activity characterized by the HOMO-LUMO 1,3-diphenyl-2-propenone energy change (Fig. 4).

The molecular orbital 38 (HOMO-1), 39 (HOMO), 40 (LUMO) and 41 (LUMO + 1) are orbital characters π. At 280

TABLE-4
RESULTS OF ZINDO/s SIMULATION AND EXPERIMENTAL

Eigen value (eV)	ZINDO/s (nm)	Experimental (nm)	Mo level	Assignment
3.977	188.94 (0.127)	191.40	38→41	π→π*
4.334	211.42 (0.105)	203.00	39→41	π→π*
5.179	242.60 (0.287)	227.80	38→40	π→π*
5.291	280.00 (1.081)	310.40	39→40	n→π*

Oscillator strength in parenthesis

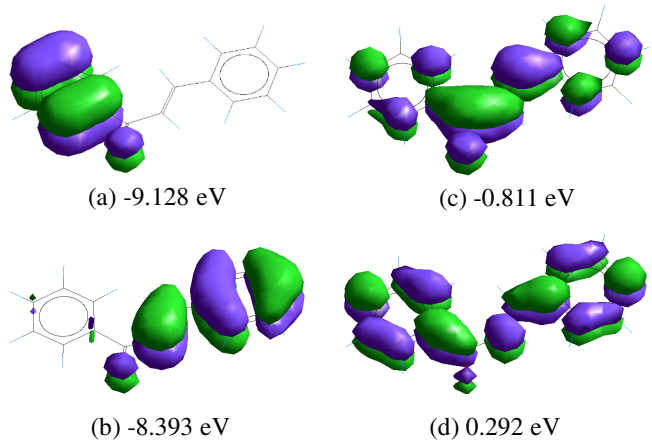

Fig. 4. Orbital molecules level (a), (b) HOMO 38, 39 and (c), (d) LUMO 40, 41

nm wavelength the 1,081 intensity shows the electronic transition at n to π* based on the wavelength shift characteristics influenced by the ketone group. The presence of lone pair electron affects the shift towards larger wavelengths.

Conclusion

The activity of the 1,3-diphenyl-2-propenone was measured as an anti-UV-B agent at a concentration of 10 ppm with the highest SPF value of 5.592. The lowest percentage of erythema transmission (% Te) is measured at 0.62 %, while the percentage of pigmentation transmission is lowest at 20 %. The electronic transition was observed on four spike UV peaks resulting from semi-empirical modeling of ZINDO/s with a molecular orbital transition π to π* at wavelengths 188.94, 211.42 and 242.60 nm. The n-molecular orbital transition to π* occurs at a wavelength of 280 nm. The molecular orbital energy under HOMO conditions is calculated at -9.128 and -8.393 eV and the electronic transition energy in the LUMO state is calculated at -0.811 and 0.292 eV.

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