Modeling Alkyl p-Methoxy Cinnamate (APMC) as UV absorber based on electronic transition using semiempirical quantum mechanics ZINDO/s calculation

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Abstract. In this research, modeling several alkyl p-methoxy cinnamate (APMC) based on electronic transition by using semiempirical mechanical quantum ZINDO/s calculation is performed. Alkyl cinnamates of C1 (methyl) up to C7 (heptyl) homolog with 1-5 example structures of each homolog are used as materials. Quantum chemistry–package software Hyperchem 8.0 is used to simulate the drawing of the structure, geometry optimization by a semiempirical Austin Model 1 algorithm and single point calculation employing a semiempirical ZINDO/s technique. ZINDO/s calculations use a defined criteria that singly excited –Configuration Interaction (CI) where a gap of HOMO-LUMO energy transition and maximum degeneracy level are 7 and 2, respectively. Moreover, analysis of the theoretical spectra is focused on the UV-B (290-320 nm) and UV-C (200-290 nm) area. The results show that modeling of the compound can be used to predict the type of UV protection activity depends on the electronic transition in the UV area. Modification of the alkyl homolog relatively does not change the value of wavelength absorption to indicate the UV protection activity. Alkyl cinnamate compounds are predicted as UV-B and UV-C sunscreen.

1. Introduction
Currently, the development research of sunscreen product has been conducted to find the new compounds with properties such as efficacious, good and does not effect on the skin. The sunscreen compound can protect skin from the effects of Ultra Violet (UV) emitted by the sun. The legal mechanism UV of a sunscreen agent is the energy absorption of UV light used for excitation of the electronic state of the compound [1]. One of the sunscreens component is octyl p-methoxy cinnamate[2].

Based on its chemical structure, the interesting part in octyl p-methoxy cinnamate are the alkyl and the benzyl chain part of the derived compound. Both of these compounds can be obtained by performing modifications on either one part of the structure or combination of some parts. The structure of alkyl p-methoxy cinnamate is presented in Figure 1.
Light absorption by molecules in ultraviolet regions depends on the electronic structure. The UV spectra of the organic compound are closely related to the transitions between electronic levels [3]. The design of sunscreen compound has been investigated in both experiments [4] and computational chemistry [5]. Simulating a sunscreen compound using a computational chemistry method has some advantages. The cost and time for spending the design process of sunscreen compound by using computational chemistry are cheap [6,7].

The use of computational chemistry methods for organic compound can be conducted with qualitative approach [5]. The qualitative approach is performed by reviewing the structure model of chemical compounds on the aspects of transition spectra on the calculations. The previous study was conducted to investigate the transition area especially on the region UV-B and UV-C [8]. Application of computational methods for using in development research was pretty much [9,10]. Modeling of sunscreen compounds has been performed by Walters, et al. [5] and also conducted by Iqmal, et al. [2] using a semiempirical calculation of molecular orbitals ZINDO to examine the activity various isoamic derived from cinnamon compounds. The application of semiempirical approach of molecular orbitals ZINDO/s has also been utilized by previous research. Mudhab [11] used this method to study the aspects of geometry and transition spectra of complex compounds Co (II)-fenantrolin and Co (II)-bipyridine. ZINDO/s method can be selected to learn the design and new model compounds of cinnamate derivatives and salicylates. The purpose of this study is to be able modeling of alkyl p-methoxy cinnamate derivatives using a semiempirical approach of molecular orbitals ZINDO/s computing in the form of spectral calculations of UV B and UV C which are the UV light areas where relatively harmful to the skin.

2. Materials
The computational chemistry equipment used in this study is a computer unit with specifications: Pentium 41.4 GHz processor, 256 MB SDRAM memory, and HD 20 GB, and HyperChem 8.0 Windows based computational chemistry software.

This computational study using the structures of alkyl p-methoxy cinnamates with alkyl type refers to the alkyl acetate material available at the chemical catalog. Type alkyl is limited to homolog C1 (methyl) until C7 (heptyl)

3. Methods
3.1 Geometry Optimization
For each compound that is used as research material, 2D structures are created with Hyperchem packages program [12]. They equipped with hydrogen atoms as each atom to complete the structure and form into a 3D structure. The process continued with the structural geometry optimization. In structural energy minimization, we obtain the structural conformation molecules which are stabilized. The method was AM1 (Austin Model 1) and the convergence limit was determined after reaching the gradient limit which is 0.01 in energy per position change. And the single calculations point energy is performed for recording the data.
3.2 Spectrum Determination
The stabilized structure was calculated by an AM1 approach with single point calculation using semiempirical ZINDO/s for generating the transition. In this calculation, the criterion which is found for the methods configuration is a single excitation (Singly excited - Cl) and the gaps HOMO-LUMO energy transition was 7. The maximum degeneration rate determined to the limit of 2. The calculation will be activated in the recording process file so the output of the calculations could be shown in detail. The data calculation results of the discontinuous spectra are in the region UV-visible wavelength. This data is used to predict the type of sunscreen compound activity.

4. Results and Discussion
Study of alkyl p-methoxy cinnamate is done by modifying the substitution of the alkyl chain. This study was to know the influence length of the alkyl chains substituent and the effect of isomer form changes for every homolog. The changes in alkyl chains include the length of it as well as in the shape of isomers. The analysis is done using an alkyl chain homolog C4 (butyl) to C7 (heptyl). The analyzed compounds are grouped and given the code as it is shown in Table 1. From each homolog that might happen, no all of them is done, as an example in homolog Hexyl; there is only four homologous. The derivatives with substantial variations in the benzyl region are not done because of the difficulty level of the synthesis compounds relatively complex. The presence of O-CH$_3$ groups in the benzyl region would complicate the synthesis procedure of alkyl p-methoxy cinnamate derivatives which is desired to substitute. The wavelength different is found because of the molecule in a pure state, while the outcome experiments analyzed has a relatively low purity [11].

The solvent effect also has the influence on the measurable uptake in more polar solvents, the red shifts uptake $\pi \rightarrow \pi^*$, and blue shifts uptake n (lone pair electron) $\rightarrow \pi^*$. The data is generated from chemical calculations of the wavelength and the intensity.

| Table 1. Structure derivative and spectrum data of alkyl p-methoxy cinnamates |
|-------------------------------------|---------------------|---------------------|
| Alkyl (R)                          | Group (C1-C7)       | Alkyl (R) structure                  |
|-------------------------------------|---------------------|-------------------------------------|
| Methyl                              | C1                  | CH$_3$•                                  |
| Propyl                              | C3                  | CH$_2$•                                  |
| Isopropyl                           | C3                  | CH$_2$•                                  |
| Isobutyl                            | C4                  | H$_2$C•                                  |
| t-butyl                             | C4                  | CH$_2$•                                  |
| n-amyl                              | C5                  | H$_2$C•                                  |
| Isoamyl                             | C5                  | H$_2$C•                                  |
| t-amyl                              | C5                  | CH•                                      |

Wavelength number (nm) with maximum intensity

292.5
290.8
289.9
291.8
290.1
292.2
292.2
292.2
292.2
| Name                  | Formula | Mass   |
|----------------------|---------|--------|
| 2,2 dimethyl propyl  | C5      | 292.2  |
| n-hexyl              | C6      | 291.5  |
| Isohexyl             | C6      | 289.7  |
| t-hexyl              | C6      | 260.6  |
| 2,2 dimethyl butyl   | C6      | 283.9  |
| 2,3 dimethyl butyl   | C6      | 289.5  |
| n-heptyl             | C7      | 290.5  |
| Isoheptyl            | C7      | 289.3  |
| t-heptyl             | C7      | 290.2  |
| 2,2 dimethyl amyl    | C7      | 290.0  |
| 2,2,3 trimethyl butyl| C7      | 290.3  |
| 3,3 dimethyl amyl    | C7      | 291.3  |
| 2,3,3 trimethyl butyl| C7      | 290.2  |
The spectrum of methyl p-methoxy cinnamate is in Figure 2. The ribbons which show the intensity of uptake rays are due to the electronic transition. The spectrum (up) represents all of the electronic transitions without showing the energy. The spectrum (bottom) has large intensity. The spectrum (up) and (bottom) are discontinuous because the chemical calculations are assumed that:
1. The compound is in a state of pure gas, so there is no effect from the other compounds.
2. The electronic transitions are from ground state to excited state.

The alkyl p-methoxy cinnamate structure is for some clusters which has simple conjugated chromophores in the benzene ring. Each of them has an electron transition type and different wavelengths. The unconjugated chromophore has the electron transition of [11]:

- O which is the transition of $n \rightarrow \sigma^*$, $\lambda = 185$ nm
- C = O which is the transition of $n \rightarrow \pi^*$, $\lambda = 300$ nm
- C = O which is the transition of $n \rightarrow \sigma^*$, $\lambda = 190$ nm

The chromophore group with no conjugated system has several auxochromes groups. They are a saturated group which bind and change the wavelength with the maximum absorption intensity. Alkyl p-methoxy cinnamate has the auxochromes group which is a methoxy group (-OCH$_3$). This compound would have a relative absorption to the UV light area and also the activity as a UV-B and UV-C sunscreen.

Changes in the form of an isomer to every alkyl homolog by the alkyl chain of the relative substituents do not cause the shifts of wavelength absorption significantly. The size of the alkyl chain is also not relatively having a good effect in the wavelength and intensity. Thus the type of UV light protection is also not influenced by the length of the alkyl chain cinnamate compounds.

The changes of straight and branch chain in alkyl homolog of methyl (C1) to heptyl (C7) show that there is no effect in the difference maximum wavelength. It could be explained because the cluster of alkyl does not contain the presence of chromophores. The chromophore is contained of double or triple bond. In the experiment, the synthesis of alkyl p-methoxy cinnamate could happen from the esterification reaction [13,14]. It would be difficult to synthesize if the chemical starting point of alkyl chain has chromophore group.

5. Conclusion
The derivative of alkyl p-methoxy cinnamate which is the alkyl of methyl, propyl, butyl, amyl, hexyl, and heptyl is a compound of UV B and UV C absorbers. Substitution of alkyl in this cinnamates compounds relatively did not give the changes of the wavelength absorption

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