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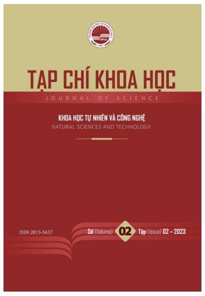

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Green synthesis of UV absorber (*E*)-2-(((4-(benzyloxy)phenyl)imino)methyl)phenol by microwave method

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Abstract

In this work, a UV absorber compound (*E*)-2-(((4-(benzyloxy)phenyl)imino)methyl)phenol was synthesized by microwave method using a two steps protocol. In the first step, *α*-(4-hydroxyphenylimino)-o-cresol (***1***) was synthesized from 4-aminophenol and salicylaldehyde by circulating under microwave heating at 60 °C for 8 minutes, the reaction yield reached 82.91 %. In the second step (*E*)-2-(((4-(benzyloxy)phenyl)imino)methyl)phenol (***2***) was synthesized from precursor (***1***) and benzyl bromide by circulating under microwave heating at 80 °C for 3 minutes, the reaction yield reached 25.08 %. The overall yield for the synthesis of UV absorber ***2*** was 20.79 %. The molecular structures of precursor (***1***) and product (***2***) were analysed by high performance liquid chromatography - mass spectrometry (LC/MS) and nuclear magnetic resonance (NMR) methods. The UV absorbance of precursor (***1***) and product (***2***) was investigated by UV absorption spectrometry. The obtained results show that product (***2***) has a higher UV absorption intensity than precursor (***1***), the UV absorption region extends from 240 nm to 390 nm, the maximum absorption peak is at the wavelength (λ_{max}) of 350 nm. The UV absorber (*E*)-2-(((4-(benzyloxy)phenyl)imino)methyl)phenol with cyclic structure, low molecular weight, and high UV absorbance has potential application as an UV absorber for greenhouse covering plastic, paint and ink systems.

Keywords: UV stabilizer, UV absorber, microwave method, green chemistry.

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1. Introduction

Polymer materials are increasingly used in daily life, they have been widely used in various fields and have gradually replaced materials such as glass, paper, and wood [1]. However, under the conditions of use, when exposed to various environmental factors such as temperature, light radiation, water, chemicals and air, polymeric materials tend to degrade and lose their physical and mechanical properties, causing the color change [2]. The destruction of polymeric materials under UV irradiation is closely related to the chemical bond strength of the polymer backbone and the energy of the UV light. UV radiation energy with wavelengths between 300 and 400 nm could break bonds in polymeric materials. The polymer molecules change from the ground state to the excited state. When the energy is large enough, it will activate for chemical reactions to take place, C - C, C - H, C - X bonds are broken, leading to polymer degradation [2-4]. The most effective solution to improve the weather resistance of polymer-based products (such as greenhouse membranes, printing inks, coatings) is to use UV-resistant additives [4,5]. These additives improve the UV stability of the polymeric materials under UV exposure conditions, thereby increasing the durability of the polymers. A UV stabilizer is a substance that prevents or slows the degradation of polymeric materials when exposed to ultraviolet light. Commercially available UV stabilizers can be divided according to their origin (inorganic and organic) or their protection mechanism (UV absorbers, quenching agents, and free radical scavengers) [5,6]. Additionally, UV stabilizers must meet other requirements such as less change in polymer properties, less impact on aesthetics, high solubility in polymers and not released during use, high heat resistant and does not evaporate or decompose during machining, odorless, tasteless, and non-toxic [2,3]. The need to use high-performance UV absorbers meeting increasingly demanding criteria therefore requires constant research and development efforts for new UV absorbers.

In this study, low molecular weight UV (*E*)-2-(((4-(benzyloxy)phenyl)imino)methyl)phenol was green-synthesized by microwave method and investigated its applicability as a UV absorber for polymers. Belonging to the Schiff base structure, compound ***1*** was synthesized and further modified in its chemical structure (product *2*) to improve its UV absorption capacity. The use of Schiff bases as the organic UV absorbers is well demonstrated in numerous reports in the literature [7-10]. The UV protection mechanism of Schiff base linked to their enol - keto transformation during UV absorption [11-12].

2. Experimental

2.1. Chemicals

Salicylaldehyde (99%), 4-aminophenol (99%), toluene (99%), and benzyl bromide (99%) were purchased from Merck (Germany). Ethanol (99.5%) and *N,N*-dimethylformamide (DMF) were provided by Chemsol (Vietnam).

2.2. Synthesis of UV absorber

The UV absorber (*E*)-2-(((4-(benzyloxy)phenyl)imino)methyl)phenol was synthesized by the microwave method using a modified Sharp R-218lW microwave oven followed a two-step process as shown in the schematic diagram in Figure 1.

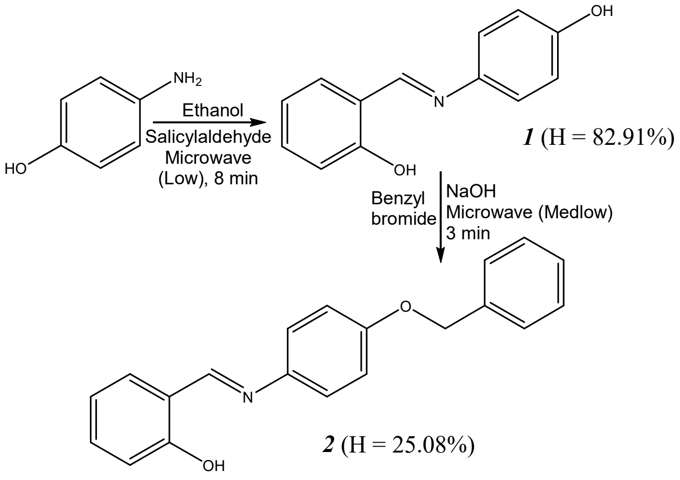

Figure 1: Synthesis of UV absorber (*E*)-2-(((4-(benzyloxy)phenyl)imino)methyl)phenol.

Synthesis of precursor α-(4-hydroxyphenylimino)-o-cresol

The precursor *α*-(4-hydroxyphenylimino)-o-cresol (***1***) is synthesized from 4-aminophenol and salicylaldehyde. Accordingly, dissolve 6.5397 g of the 4-aminophenol in 80 mL of absolute ethanol, then add 6.30 mL of salicylaldehyde to this solution. Circulate the reaction mixture in a microwave oven at 60 °C for 8 min using the low power level setting. After the reaction, the solution was allowed to cool at room temperature. Crystallize the product by slowly adding the reactant solution to 700 mL of distilled water under stirring (300 rpm) to form yellow-orange crystals. Filter for crystals and purify the product by dissolution/recrystallization in distilled water (700 mL), in ethanol (80 mL), and DMF (30 mL), sequentially. The purified product was vacuum-dried for 2 hours at 60 °C to obtain 10.5965 g of the precursor product (***1***) orange yellow, fine powder, with a reaction yield (H) of 82.91 %.

Synthesis of UV absorber (E)-2-(((4-(benzyloxy)phenyl)imino)methyl)phenol

UV absorber (***2***) was synthesized from precursor (***1***) according to the following procedure: Dissolve 2.1305 g of precursor (***1***) in 30.0 mL of ethanol to obtain solution A. Dissolve 0.2065 g NaOH to 20 mL ethanol yields solution B. Transfer solutions A and B to a 500 mL flask, add to the mixture 1.20 mL benzyl bromide and perform the reaction at 80 °C in the microwave oven for 3 min using the medium power level setting. After the reaction, let the mixture cool to room temperature. The product that crystallized at room temperature was filtered and washed on a Buchner funnel with 7.0 mL of absolute ethanol. The obtained product (***2***) is yellow-orange, in the form of flake-like and was stored in a desiccator. The reaction efficiency reached 25.08 %. The overall yield of the two-step process for the synthesis of UV absorber ***2*** was 20.79 %.

2.3. Analysis of the chemical structure and UV absorption properties of the product

Chemical structure and product purity were analyzed by liquid chromatography coupled to mass spectrometry (LC/MS, full scan mode, using acetonitrile with 0.1% formic acid solvent) using an microTOF-Q instrument (Bruker Daltonics, Germany) and nuclear magnetic resonance spectroscopy (^{1}H NMR, ^{13}C NMR) using a Bruker Avance 600 DRX instrument (Bruker, USA). The UV absorbance of the product was analyzed by UV absorbance spectrometry using a V-670 UV–Vis-NIR spectrophotometer (JASCO, Japan). Melting temperatures of precursors and products were measured using an SMP30 instrument (Stuart, UK). Thin layer chromatography (TLC) process was involved on silica gel 60 F254 plates (Merck).

3. Results and discussion

3.1. Chemical structure of precursor (1)

The obtain product after purification was preliminarily analysed by TLC using toluene/methanol 7:3 (v/v) as eluent, the results showed that only a yellow circular streak without tail pulling (Rf = 0.59). The LC/MS analysis results of precursor (***1***) are presented in Figure 2. The LC of compound (***1***) appeared only a single peak on the chromatogram showing that the product after the reaction contains only one compound. The MS spectrum results showed that the obtained compound has a molecular weight of 213. The chemical structure of the precursor was intensively studied by NMR method in $CDCl_3$ solvent.

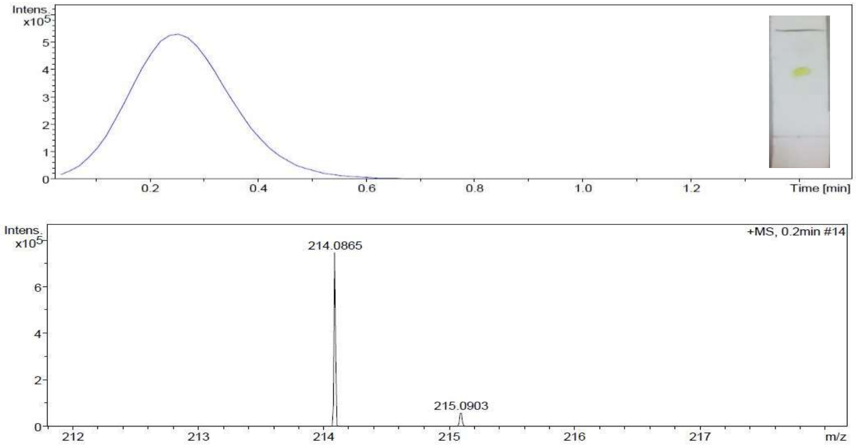

Figure 2: LC/MS spectrum of precursor (***1***), the insert image is a thin-layer chromatography image.

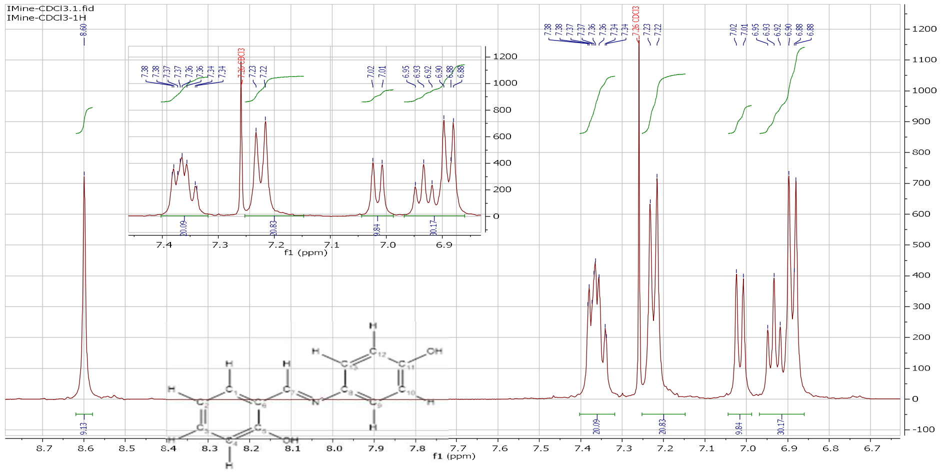

Figure 3: ^{1}H NMR spectrum of precursor (***1***).

Table 1: Comparison of theoretical and experimental chemical shifts for precursor (***1***)

Proton(s) in molecule	**Chemical shift *δ* (ppm)**		**Number of protons**	**Peak multiplicity (*s, d, t*)**
	Theorical	Experimental		
1	7.66	7.34	1	*dd*
2	7.08	6.93	1	*td*
3	7.52	7.37	1	*td*
4	7.02	7.02	1	*dd*
7	8.87	8.60	1	*s*
9,13	7.22	7.22	2	*dd*
10,12	6.99	6.89	2	*dd*

The LC/MS and ^{1}H NMR analysis results confirmed that the compound (***1***) was of high purity and was identified as *α*-(4-hydroxyphenylimino)-o-cresol.

3.2. Chemical structure of product (2)

Similar to compound (***1***), the product (***2***) obtained in the second stage of the UV absorber synthesis process was previously analysed by TLC for purity and chemical structure analysis by LC/MS and NMR methods. The product ***(2)*** was preliminarily analysed by TLC using toluene/methanol 7:3 (v/v) as eluent, the results showed that only a yellow round spot without trailing tail with Rf = 0.97. The LC/MS spectrum of product (***2***) is presented in Figure 4.

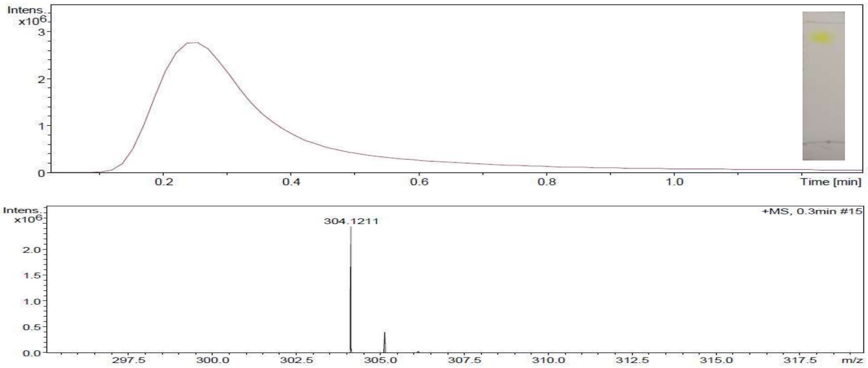

Figure 4: LC/MS spectrum of the product (***2***), the inserted image is a thin-layer chromatography image

The ^{1}H-NMR spectrum of compound (***2***) in $CDCl_3$ solvent show a total of 11 resonances corresponding to 16 protons (Figure 5). As can be seen on the ^{1}H NMR spectrum, there is a signal of protons in the $-CH_2-O-$ group with δ = 5.12 ppm, this is the signal of proton H-14 which is a new signal compared to that of compound (***1***). In addition, there are proton positions 16, 20; 17, 19 and 18 are the new proton signals of (***2***). Two pairs of protons H-16, H-20 and H-17, H-19 have spin - spin interactions with each other. The H-16 and H-20 protons (7.45, 2H, *dd*, *J* = 7.5 Hz) showed a larger displacement than the H17 and H19 protons because they are located near the -CH_2-O- group, which is an electron withdrawing group and thus causes a resonates at low magnetic fields. At the same time, H-17 and H-19 (7.38, 2H, *td*, *J* = 7.5 Hz) have a spin-spin interaction with H-18 (7.35, 1H, *td*, *J* = 7.5 Hz). A comparison of the theoretical and experimental chemical shifts of (***2***) is presented in Table 2.

Table 2: Comparison of theoretical and experimental chemical shifts of (***2***)

Proton(s) in molecule	**Chemical shift *δ* (ppm)**		**Number of protons**	**Peak multiplicity (*s, d, t*)**
	Theorical	**Experimental**		
1	7.66	7.39	1	*Dd*
2	7.08	6.94	1	*Td*
3	7.52	7.41	1	*Td*
4	7.02	7.05	1	*Dd*
7	8.87	8.62	1	*S*
9,13	7.22	7.27	2	*Dd*
10,12	6.99	7.03	2	*Dd*
14	5.16	5.12	1	*S*
16,20	7.47	7.45	2	*Dd*
17,19	7.38	7.38	2	*Td*
18	7.38	7.35	1	*Td*

The ^{13}C NMR spectrum of product (***2***) is shown in Figure 6. The positions of carbon 9, 13 and 10, 12 are symmetrical through the C=N and C-O groups on the benzene ring, so they have the same displacement. The same results were observed for carbons 16, 20 and 17, 19. The comparison of theoretical and experimental chemical shift values for each carbon of product (***2)*** are presented in Table 3. The LC/MS, ^{1}H NMR, and ^{13}C NMR results confirmed that the UV absorber (*E*)-2-(((4-(benzyloxy)phenyl)imino)methyl)phenol of high purity was successfully synthesized by microwave method.

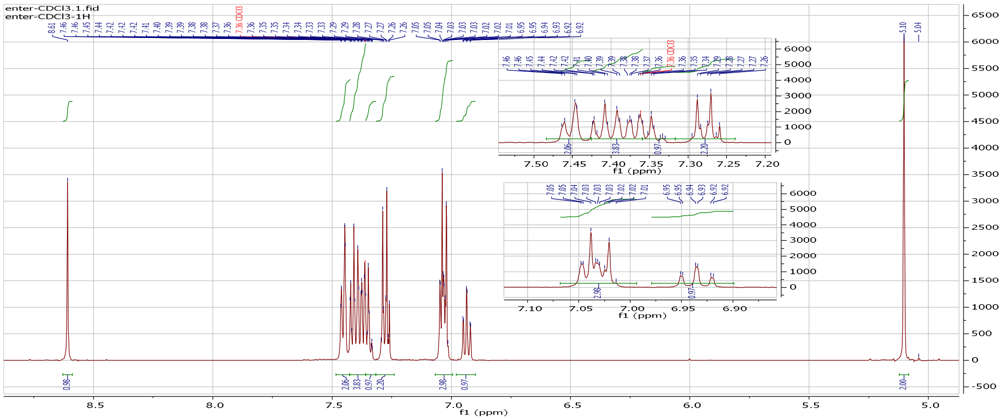

Figure 5. ^{1}H NMR spectrum of product (***2***).

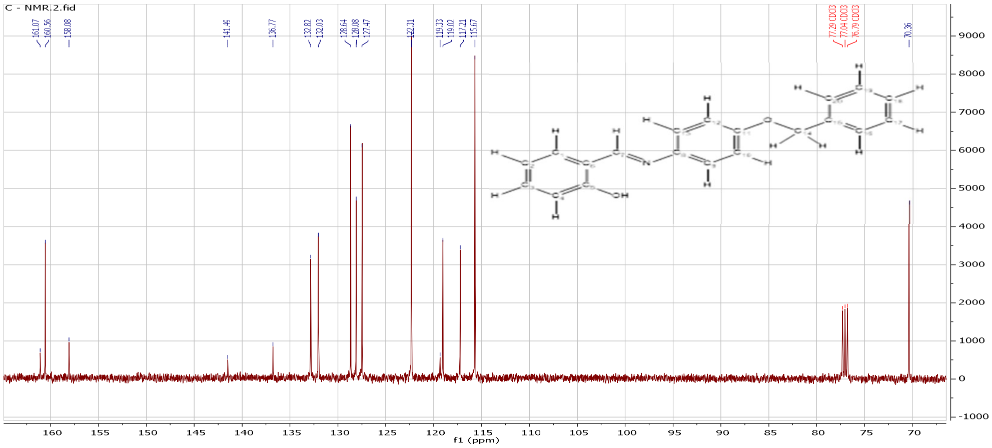

Figure 6: ^{13}C NMR spectrum of product (***2***).

Table 3: Comparison of theoretical and experimental chemical shifts of carbon of product (***2***)

Carbon (s) in molecule	**Chemical shift *δ* (ppm)**	
	Theorical	**Experimental**
1	132.1	132.1
2	121.4	119.3
3	132.4	132.8
4	117.8	117.2
5	161.1	161.1
6	120.5	119.0
7	160.0	160.5
8	144.6	141.4
9, 13	122.5	122.3
10, 12	117.2	115.7
11	157.0	158.2
14	70.8	70.4
15	136.7	136.6
16, 20	127.1	127.5
17, 19	128.9	128.7
18	127.6	128.1

The UV absorption property of product (***2***) was analysed and compared with precursor (***1***) by UV absorption spectrometry method. In addition, the applicability of the product is also evaluated via the melting point values.

3.3. UV absorption properties of the product

The results of fusion heat analysis showed that product (***2***) has a melting point of 129 °C, lower than that of precursor (***1***), which has a melting point of 137 °C. This can be attributed to the reduction of the intermolecular interaction in product ***2*** compared to that of precursor ***1,*** which is related to the decrease in the number of OH groups (from two -OH groups in molecule ***1*** decreased to one -OH group in molecule ***2***).

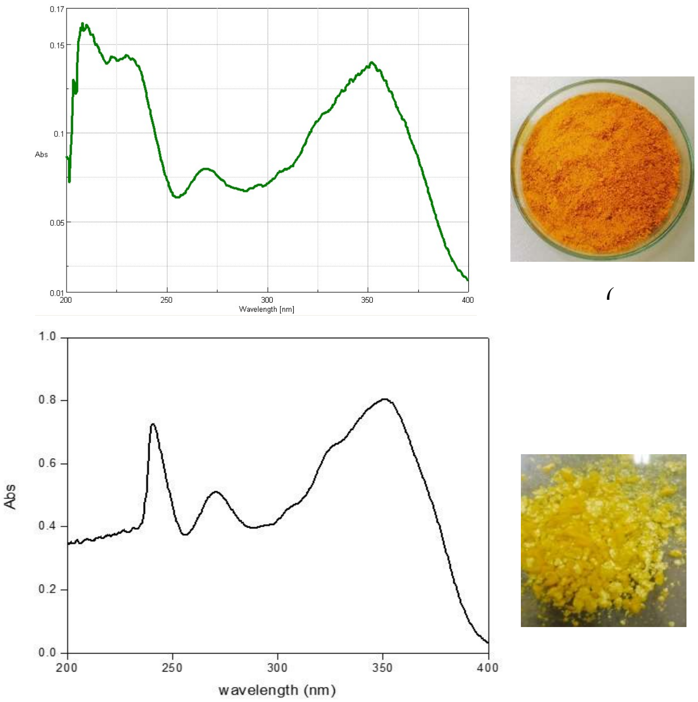

Figure 7: Comparison of UV absorption spectrum of precursor (***1***) and product (***2***).

As can be seen in the Figure 7, precursor (***1***) absorbs UV in the 200 - 400 nm region with peak absorption peaks (λ_{max}) at 210 nm and 348 nm. Product (***2***) has a wide UV absorption range from 240 nm - 390 nm (covering two regions UVA 99 % of the sunlight and UVB spectrum), the strongest absorption at wavelength λ_{max} = 350 nm. In the wavelength range from 240 nm to 400 nm, the UV absorption intensity of product (***2***) is increased (about 5.8 times at 350 nm) compared with precursor (***1***), indicating that the UV absorbance of product (***2***) is higher than precursor (***1***). The high UV absorbance coupled with the low melting point of the product (***2***) promises its application as a UV absorber for UV durable printing inks, paint coatings, and agricultural films.

4. Conclusions

UV absorber (*E*)-2-(((4-(benzyloxy)phenyl)imino)methyl)phenol has been successfully synthesized by a two-stage microwave method. The obtained product has a melting temperature of 129 °C, high UV absorbance in the range of 240 nm - 390 nm, peaking at 350 nm, promising applicability as a UV absorber for paint systems, printing inks and UV durable agricultural films. In addition, the microwave green synthesis method helps to shorten the reaction time, minimize environmental pollution, give high product selectivity and is convenient when synthesizing products on an industrial scale compared to other methods.

Declaration of Competing Interest

The authors declare no competing interests.

Author contributions

Thi Kieu Khanh Nguyen, Anh Thu Nguyen, Pham Anh Vu Ho main contributions of the article.

Le Viet Hai participated in giving ideas and editing scientific content of the article.

Nguyen Ngoc An, Huynh Le Thanh Nguyen, Thanh Thien Co, Hoang Thai Nguyen, Quang Ton That contributed on data analysis and testing.

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