

## Identification of Two Hetero-Substituent-Aromatic Isomers of -4- and 7-Hydroxy Coumarin with the Belousov-Zhabotinsky Oscillator

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In this article, we presented an innovative work of distinguishing the two different positional hetero-substituents-aromatic isomers i.e. 4-hydroxycoumarin (4-HC) and 7-hydroxycoumarin (7-HC) on their perturbation effect by a novel analytical Belousov-Zhabotinskii (BZ) oscillator. In such BZ oscillator, the tetra-aza-macrocyclic copper complex ( $[\text{CuL}](\text{ClO}_4)_2$ ) was used in which the ligand L is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11 diene. Experimental data confirmed that, by discrete injection of these two isomers (4-HC and 7-HC) into the active BZ system with equal concentrations reflected in their inhibition time ( $t_{\text{in}}$ ), but the  $t_{\text{in}}$  produced by 4-HC was higher than the  $t_{\text{in}}$  initiated by 7-HC. The interesting feature is that, with increasing concentrations ( $9.0 \times 10^{-5}$  to  $3.6 \times 10^{-4}$ ) of 4-HC constantly increase the  $t_{\text{in}}$  and decreased the oscillation number (N) after the regeneration of oscillation. Whereas, the upsurge concentrations of 7-HC didn't change the  $t_{\text{in}}$  but reduced the N after regeneration of oscillation. Thus, the two isomers were identified. Based on the mechanistic approach of FKN (Field-Koros-Noyes) model, the reaction perturbation mechanism was discussed. A fleeting description is that both 4-HC and 7-HC isomers were oxidized by  $\text{BrO}_2^\bullet$  intermediate radical (which produce during the course of reaction) into salicylic acid and quinone respectively and the system was temporary freeze ( $t_{\text{in}}$ ) as well. The products (salicylic acid and quinone) were identified by infra-red and Ultra-Visible spectroscopies.

**Keywords:** Belousov-Zhabotinsky; Chemical Oscillation; Isomers Identification; Hydroxycoumarin; Intermediate Species; Perturbation effect

### 1. INTRODUCTION

In analytical chemistry, a significant task is the identification of isomers of compounds: having a similar chemical formula but the response in different behaviors. That why, their selectivity is highly

important in the practices analysis more especially in food, and medicinal or pharmacology industries [1-3]. Recently, it is found commonly in food or medicine manufacturing industries for using different isomers of same compounds in productions of same medicines which is mostly reflected in health hazards, side effects or ignition of other kinds of diseases in the host. Because it is not necessary that all isomers of the same compounds may have the same functions for the same cure. Therefore making food or medicines from wrong isomers will take lives. For example, the cis-plating isomer is used against various types of cancers (lungs, bladder, breast, etc.) but the trans-plating has no beneficial pharmacological activity [4]. Similarly, L-dopa working against Parkinson's disease while L-dopa is harmful to white blood cells. Thus, the aim of this articles is not only conveying the awareness regarding the correct selection of isomers for the betterment of mankind but also provide a new methodology of analyzing isomers of a compound by a chemical oscillating system with a simpler setup, lower detection limits and less price than the other instrumental techniques.

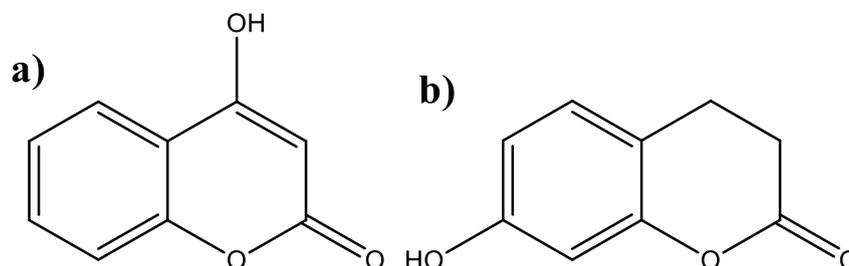
According to the literature, various techniques were utilized for the identification of the isomers such as high-performance liquid chromatography (HPLC) [5, 6, 7], capillary electrophoresis [8, 9, 10], single-molecule force spectroscopy [11], and ultra-violet (UV-Visible) spectroscopy [12]. Although, all of these techniques are more convenient for isomers identification, because of their high cost and some technical malfunctions give privilege to over proposed method. For example, in utilizing HPLC and capillary electrophoresis an excessive amount of the solvent is consumed in columns. UV-spectroscopy lack of selectivity, sensitivity and limited to UV-Vis absorbing compounds. Thus, a desire for an analytical tool is needed which overcomes the limitation of the above techniques. In the current paper, we presented a novel analytical technique based on oscillating chemical system (Belousova-Zhabotinsky) for the identification of the isomers, which is more prominent than instrumental techniques by some features (operate at low temperature, in an aqueous medium, a high range of detection limits and low cost as well).

Among the hundreds of chemical oscillator, the most well-known oscillators are the Briggs-Rauscher (BR) system [13-14] Belousov-Zhabotinsky (BZ) system [15-17] and Bray-Liebafsky (BL) system [18-20]. These oscillators were widely used for qualitative analysis i.e. determination of various types of the ions [21, 22], evaluating of antioxidant activity of various compounds [23, 24] and utilized to some extent for organic compounds [25-27] as well.

Recently, our group has successfully utilized oscillating chemical systems (BR and BZ) for identification of aliphatic isomers [28], cyclic isomers [29] and homo substituent (1 or 2) aromatic isomers [30-32]. The results of isomers identification of our published papers have quite differed from each other. Because of interesting outcomes in the field of isomers identification by using oscillating systems need to further apply to the identification of other kinds of isomers. Thus, we extended the role of the oscillating system by identifying hetero-aromatic isomers (4-Hydroxycoumarin (4-HC) and 7-Hydroxycoumarin 7-HC) for the first time in the current research.

In this paper, Cu-complex catalyzed BZ oscillator was used to distinguished the two isomers of hetero-aromatic isomers i.e. 4-HC and 7-HC (scheme 1) by their perturbation effect. The experimental results have shown that the addition of both the additives into the active BZ system could cause the inhibition time ( $t_{in}$ ) but the  $t_{in}$  produced by 4-HC has higher than the  $t_{in}$  initiated by 7-HC. Furthermore, as the concentration of 4-HC were increase, the  $t_{in}$  of the system was increase but the increasing

concentration of 7-HC into the system didn't increase the  $t_{in}$ . In short, the  $t_{in}$  produced by 4-HC is directly proportional to their concentration while the produce  $t_{in}$  by 7-HC is indirectly proportional to the concentration of 7-HC. Meanwhile, we have claimed that in both cases the  $t_{in}$  was due to the involvement of the intermediate species ( $HOO^*$ ). During the course of the reaction, such intermediate species oxidized the additives into their respective products (quinone and salicylic acid). The well-known oscillating FKN mechanism was used to construct the perturbation mechanism.



**Scheme 1.** (a) Structure of 4-hydroxycoumarin; (b) 7-hydroxycoumarin

## 2. EXPERIMENTAL

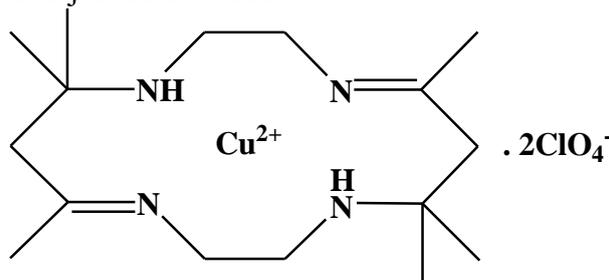
### 2.1. Apparatus

Experimental assembly of BZ system consist a 50ml beaker (in which 40 ml BZ mixture was poured) and two electrodes i.e. platinum electrode (Shanghai China, type 213) was used as working electrode while saturated calomel (Shanghai China, type 213) act as reference electrode have a salt bridge, which consists of 0.04 M of  $Na_2SO_4$  crystals of KCl, acting as to display the change in potential. These two electrodes were immersed into the BZ mixture (40 ml) and connected to PC though amplifier (Vernier soft technology, U.S.A) and Go!link sensor interfere (Vernier soft technology, U.S.A). The data of potential vs time were analyzed in PC through software logger lite data-acquisition programmer. In overall experiments, the oscillatory mixture was stirred at 550 rpm using a magnetic stirrer (model 79-3). Aliquots were injected into mixture via a micropipette. The cyclic-voltammetric base station (Shanghai Chendua instruments Ltd., China, model CH1660) was used to indorse the reduction and oxidation reaction among additives and intermediate radical. While the products were identified through UV (Shimadzu, Japan, model UV-1750) spectrometer and FT-IR (Thermo Nicolet Corporation, U.S.A).

### 2.2. Chemicals

All chemical reagents i.e.  $H_2SO_4$  (Aldrich, China),  $NaBrO_3$  (Sinopharm chemical reagent, China) and malic acid (Aladdin, China), 4-HC (Aladdin, China), and 7-HC (Aladdin, China), were purchased commercially and used with no additional characterization except Cu-complex catalyst (Scheme 2) which was synthesized according to literature [33] and recognized by Infrared spectroscopy, and elemental analysis. The 1.0 M  $H_2SO_4$  solution was used to prepare 2.0 M malic acid,  $6.40 \times 10^{-1}$  M

NaBrO<sub>3</sub>, and 1.74 × 10<sup>-3</sup> M ([CuL](ClO<sub>4</sub>)<sub>2</sub>) solutions. The different concentrations of analyzed samples (4-HC and 7-HC) were prepared just before used.



**Scheme 2.** Structure of [CuL](ClO<sub>4</sub>)<sub>2</sub>

### 2.3. Procedure

The oscillating solution (40 ml) was put into a beaker by the following order; 28.50 ml of 1.00 M H<sub>2</sub>SO<sub>4</sub>, 1.50 ml of 6.40 × 10<sup>-1</sup> M NaBrO<sub>3</sub>, 4.50 ml of 2 M Malic acid; 6.5 ml of 1.74 × 10<sup>-3</sup> M [CuL](ClO<sub>4</sub>)<sub>2</sub>. Both Pt- and SCE electrodes were put into the beaker and record the potential vs time in PC. For perturbation experiments, various amounts of additives were used and observed the phenomenon.

## 3. RESULTS AND DISCUSSION

### 3.1. Unperturbed BZ typical oscillation

The unperturbed BZ typical oscillation (Fig1a) was achieved by mixing the reagents into the above order. Throughout oscillation, the periodic changing of the solution color from red to orange was observed, indicating the below continuous oxidation and reduction of catalyst in the reaction.

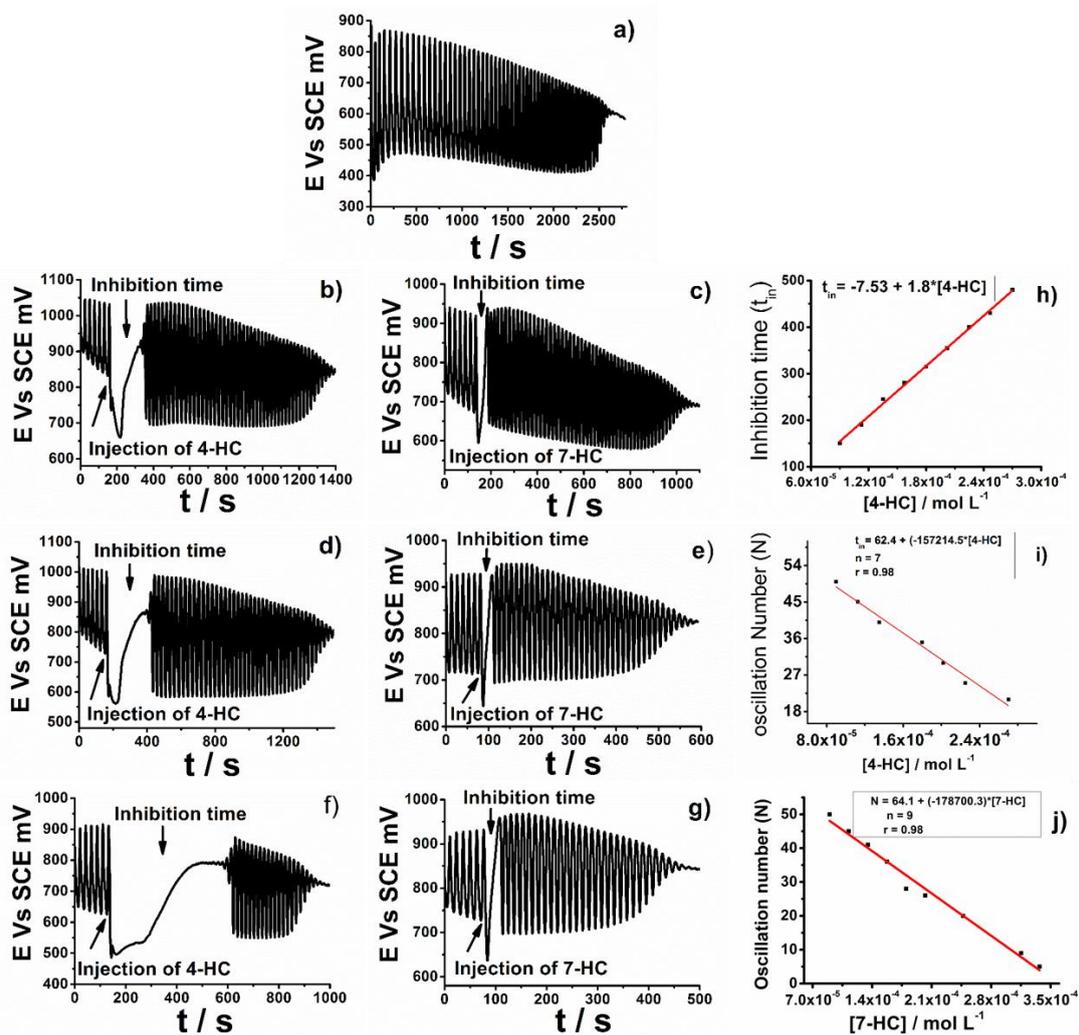


### 3.2. Perturbed BZ typical oscillation (4-HC and 7-HC)

In order to distinguish between two isomers, the concentration range was testified from 0.90 M to 0.1 M (final concentration is 9.0 × 10<sup>-5</sup> M to 1.0 × 10<sup>-4</sup> M). By the addition of 9.0 × 10<sup>-5</sup> M of 4-HC into the system could produce longer inhibition time (*t*<sub>in</sub>) along with the regeneration of small (few cycles) and followed by higher oscillation amplitude as shown in the Figures 1b. Whereas, the injection of the same amount of the same concentration of 7-HC (9.0 × 10<sup>-5</sup> M) produce shorter *t*<sub>in</sub>, only the increase regeneration of oscillation amplitude as indicated in Figure 1c. The interesting features are that as the concentrations of 4-HC were increased into the system, the *t*<sub>in</sub> of the system was increased but with a decrease in the reproduction of oscillation number (N) after *t*<sub>in</sub> (Figure 1d,f). While, the increasing concentration of 7-HC into the system couldn't increase or decrease the *t*<sub>in</sub> but just reduce the oscillation

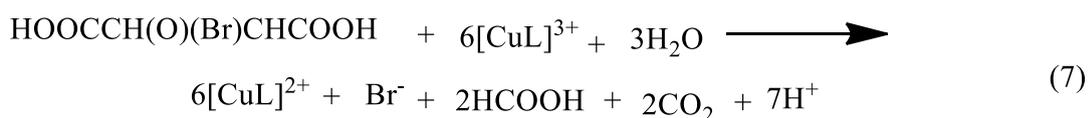
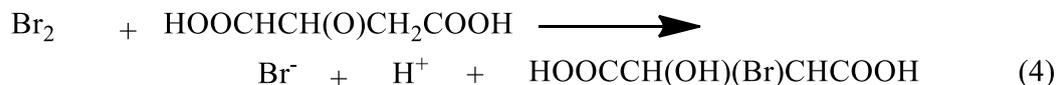
number after regeneration of oscillation after a constant  $t_{in}$  (Figure 1e,g). Thus, linear relationships were achieved between the concentrations of 4-HC vs  $t_{in}$  (Figure 1g,h); concentrations of 4-HC vs N (Figure 1i), and concentration of 7-HC vs N (Figure 1j) in their concentration range from  $9.0 \times 10^{-5}$  to  $3.15 \times 10^{-4}$  M.

Thus, these two isomers are shown too identified by their perturbation effects towards BZ system oscillating system and providing evidence of a new way of isomers identifying methodology by oscillation system with a simpler setup, low price and, small detection limits. Such a methodology will also applicable for identifying other kinds of isomerids as well.



**Figure 1.** (a). Unperturbed oscillation; (b) Perturbed oscillation by injection of  $9.0 \times 10^{-5}$  M 4-HC; (c). Perturb oscillation by injection of  $9.0 \times 10^{-5}$  M 7-HC; (d). Perturb oscillation by Injection of  $1.8 \times 10^{-4}$  M 4-HC; (e). Perturb oscillation by Injection of  $1.8 \times 10^{-4}$  M 7-HC; (f). Perturb oscillation by Injection of  $2.7 \times 10^{-4}$  M 4-HC; (g). Perturb oscillation by Injection of  $2.7 \times 10^{-4}$  M 7- HC; (h). Linear relationship between 4-HC vs  $t_{in}$ ; (i). Linear relationship between 4-HC vs N; (j). Linear relationship between 4-HC vs  $t_{in}$ ; (i). Linear relationship between 7-HC vs N. Common Conditions; 28.5 ml of  $6.76875 \times 10^{-1}$  M  $H_2SO_4$ ; 1.5 ml of  $2.4 \times 10^{-2}$  M  $NaBrO_3$ ; 4.5 ml of  $2.1375 \times 10^{-1}$  M Malic acid; 5.5 ml of  $2.37875 \times 10^{-3}$  M  $[CuL](ClO_4)_2$ ;  $T = 26^\circ C$ .

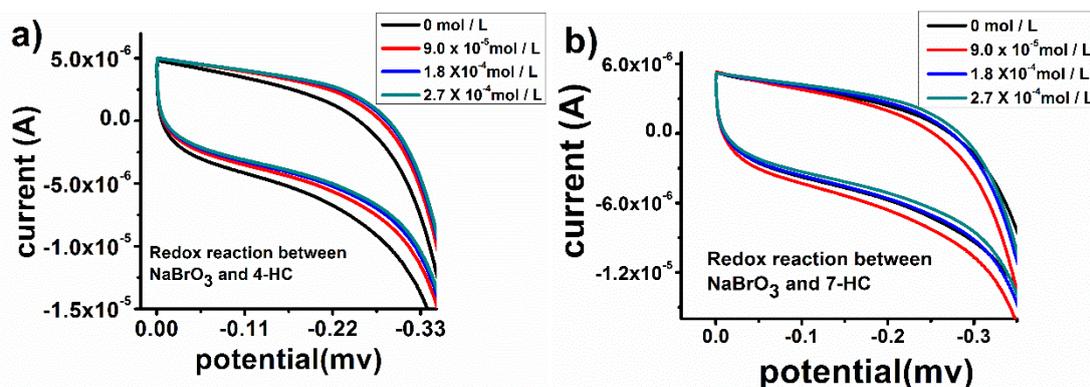
### 3.3 Mechanism for the BZ oscillating reaction



The mechanistic approach of the chemical oscillating systems (BZ) is highly complex because of the involvement of various kinematic steps, intermediate species and free radicals [34]. In each era, simplification of the oscillatory mechanism remained the center of attention, therefore various attempted has been made for achieving a well-known FKN (Field, Koros and Noyes) mechanism for metal-catalyzed BZ oscillating system [35]. With the used of tetra-aza-macro-cyclic Cu-complex catalyst, the novel FKN mechanism was modified into the below 7 oscillatory steps for BZ oscillating system [36,37,38]. In such a particular system, the oscillation was sustain due to the interconversion of single electron between  $[\text{CuL}]^{2+}$  and  $[\text{CuL}]^{3+}$ .

### 3.4 Cyclic voltammetry (CV) experiments

The cyclic voltammetry experiments were performed in order to confirm the redox reaction between the BZ reagents and isomers (4-HC and 7-HC). Such experiments was carried out in the following media in presence and absence of additives; (i) 38.5 ml of  $1.77 \times 10^{-2}$  M  $\text{H}_2\text{SO}_4$  + 1.5 ml of  $6.4 \times 10^{-2}$  M of  $\text{NaBrO}_3$ ; (ii) 2.3 ml of  $24 \times 10^{-1}$  M malic acid + 38.5 ml of  $1.77 \times 10^{-2}$  M  $\text{H}_2\text{SO}_4$  (iii) 35 ml of  $1.77 \times 10^{-2}$  M  $\text{H}_2\text{SO}_4$  + 5.5 ml of  $1.74 \times 10^{-3}$  M  $[\text{CuL}](\text{ClO}_4)_2$ . Although the cyclic voltammograms confirmed the only redox reaction between additives and  $\text{NaBrO}_3$  (as shown in Figure 2). Actually, the additives were oxidized by  $\text{BrO}_2^\bullet$  intermediate radical which was produced during the course of reactions. The  $\text{BrO}_2^\bullet$  radical was supposed to be formed by the decomposition of sodium bromate.



**Figure 2.** (a) Cyclic voltammogram of NaBrO<sub>3</sub> with 4-HC; (b) Cyclic voltammogram of NaBrO<sub>3</sub> with 7-HC; Common condition = 0.100 M H<sub>2</sub>SO<sub>4</sub> = 38.50 ml; 0.64 M NaBrO<sub>3</sub> = 1.50 ml.

### 3.5 Products Identification

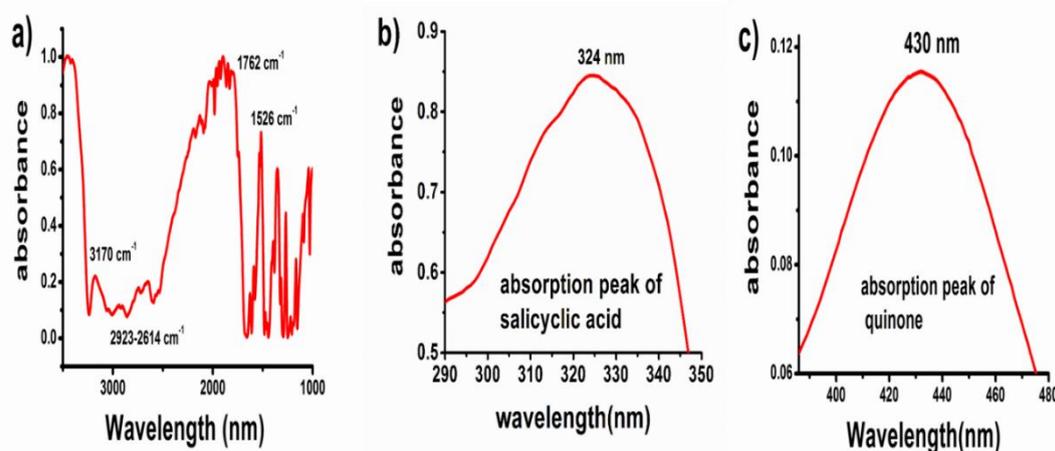
It is our claim that in the BZ system, the 4-HC and 7-HC were oxidized by BrO<sub>2</sub><sup>•</sup> radical into salicylic acid and quinone as indicated in reaction 8 and 9 respectively. According to the recently published literature [39], the 4-HC was oxidized into salicylic acid. Herein, we confirm by Infra-Red and Ultra-Visible spectroscopies that the 4-HC was oxidized into salicylic acid.

For IR experiment, a solid product was required, so for this purpose we used a higher concentration of 4-HC (3.5ml of a 2M) with acidic solution of KIO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> in order to get oxidation product. We did not use the malic acid and catalyst in the mixture because it didn't show a redox reaction with 4-HC during CV experiment, and secondly, the presence of malic acid would create confusion in separating the oxidized product from 4-HC with that of malic acid because both of them are organic compounds. In particular circumstance, a huge interference due to malic acid will be noticed in analyzing the IR spectrum (used to identified product) of the oxidized product. Absence of malic acid will solve this problem. The obtained solid was recrystallized and performed IR spectrum as shown in Figure 3 (a). At 3170 cm<sup>-1</sup> is the characteristic peak of C-H aromatic bond. The consecutive range lies at 2923-2614 cm<sup>-1</sup> range shown the overall carboxylic acid while the OH peak in carboxylic acid satisfied the peak at 1762 cm<sup>-1</sup>. Furthermore, the 1526 cm<sup>-1</sup> peak represents the corresponding peak of C=C in aromatic. Thus, the above IR results shown that the oxidized peaks from 4-HC are salicylic acid.

The oxidized product (salicylic acid) from 4-HC was further confirmed by ultra-violet (UV) technique. To UV-experiment, solution  $9.0 \times 10^{-5}$  M of 4-hydroxycoumarin was prepared within 6ml of  $6.4 \times 10^{-1}$  M NaBrO<sub>3</sub> and 34 ml of  $1.2 \times 10^{-5}$  M H<sub>2</sub>SO<sub>4</sub>. The solution was kept for 1hr. Then 1ml from such mixture was taken in UV-cuvette and the experiment was run. The obtained spectrum was shown in Figure 1b. The spectrum has a maximum absorption peak at 324 nm for salicylic acid which is closer to the value (310 nm) of reported [40] literature for salicylic acid.

The product formation (quinone) from 7- HC within the BZ system was confirm by UV - spectroscopy (model UV-1750, Shimadzu, Japan). In 2001 it has been reported [41] that the absorption quinone peak is lying between the 350cm<sup>-1</sup> to 450cm<sup>-1</sup>. In particular experiment, the mixture of  $9.0 \times 10^{-5}$  M 7-HC, 38.5ml of 1M H<sub>2</sub>SO<sub>4</sub> and 1.5ml of NaBrO<sub>3</sub> was prepared and kept for 1hr. Then, 1ml from

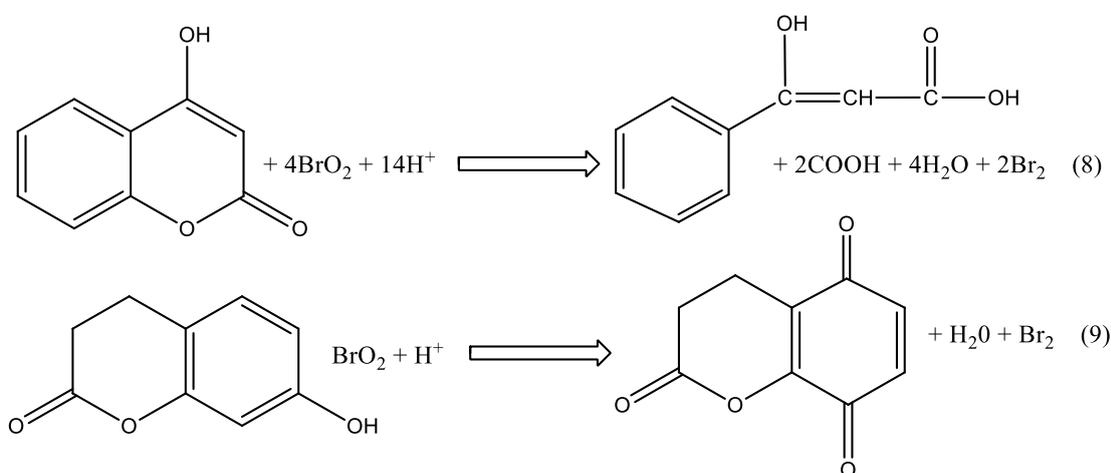
such mixture was taken in the cuvette and obtained UV spectrum as indicated in Figure 3(c). The maximum absorption peak at 400 nm was noticed which is the agreement peak of quinone.



**Figure 3.** (a) IR-spectrum of oxidized product (salicylic acid) from 4-HC; (b) UV-spectrum of 4-HC in the presence of H<sub>2</sub>SO<sub>4</sub> and NaBrO<sub>3</sub>; (c) UV-spectrum from oxidation of 7-HC in the presence of H<sub>2</sub>SO<sub>4</sub> and NaBrO<sub>3</sub>

### 3.6. Mechanism explanation of 4-HC and 7-HC in BZ reaction

When the additives (4-HC and 7-HC) were added, the system was ceased by the consumption of BrO<sub>2</sub><sup>•</sup> free radical, which was regenerated after the complete conversion of additives into their respective products with a byproduct of Br<sub>2</sub> (reactions 8 and 9). The increased amount of Br<sub>2</sub> pushed the reaction 3 in the backward direction and the amount of HOBr was increased which reverse reaction 2, thus HBrO<sub>2</sub> was enriched into the system. Such a higher concentration of HBrO<sub>2</sub> boosted reaction 4 in the forward direction to produce BrO<sub>2</sub><sup>•</sup>. Due to reaction 4, the oxidation and reduction process of reaction 6 and 7 were resumed and the oscillation was again regenerated.



#### 4. CONCLUSION

For the first time, distinguishing methodology between the two hetero substituent-aromatic isomers (4-HC and 7-HC) by using the Belousov-Zhabotinsky oscillating system as an analytical tool was reported in this paper. Perturbation behaviors of these isomers are quite different, although both isomers produced inhibition time. The inhibition time caused by 4-HC is larger than the inhibition time originated by 7-HC. Besides this, different products were obtained from the oxidation of these isomers by  $\text{BrO}_2^\bullet$ . The 4-HC and 7-HC was oxidized into salicylic acid and quinone respectively which were confirmed through IR and UV spectroscopic techniques.

#### ACKNOWLEDGEMENTS

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#### CONFLICT OF INTEREST

All authors has declare no conflict of interest.

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