Bulgarian Chemical Communications, Volume 48, Special C (pp. 20–26) 2016

Synthesis, spectroscopic studies and electrochemical properties of Schiff bases derived from 5-chloro-2-hydroxybenzaldehyde with methyl 2-amino-6-methyl-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylate

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Received June 26, 2016, Revised September 10, 2016

Schiff base; methyl 2-((5-chloro-2-hydroxybenzylidene)amino)-6-methyl-4,5,6,7-tetrahydrothieno[2,3-c]pyridine-3-carboxylate was synthesized by the reaction of methyl 2-amino-6-methyl-4,5,6,7-tetrahydrothieno[2,3-c]pyridine-3-carboxylate with 5-chloro-2-hydroxybenzaldehyde in excellent yield. This compound was characterized by elemental analysis, NMR (^{1}H and ^{13}C-APT), FT-IR and X-ray diffraction methods. The electrochemical behavior of Schiff base was investigated using cyclic voltammetry (CV), controlled potential electrolysis and chronoamperometry (CA) techniques. The number of electrons transferred (n), diffusion coefficient (D) and standard heterogeneous rate constants (k_s) were also determined by electrochemical methods.

Key words: Schiff base, 2-aminothiophene, X-ray diffraction, electrochemical behavior

INTRODUCTION

Multi-substituted 2-aminothiophenes are a kind of important privileged structures used as a scaffold to construct a series of natural products. In particular, 2-aminothiophene derivatives have been demonstrated in a number of applications such as in pesticides, dyes [1], agrochemical applications[2,3] and pharmaceuticals [1,4], anti-inflammatory [5,6], analgesic, antidepressant, antioxidant [7], antitumor [8], antimicrobial, antibacterial [9], anthifungal [10] and anticonvulsant activities [11-19]. Substituted 2-aminothiophenes are active as allosteric enhancers at the human A1 adenosine receptor [3,20,21]. Some of them are serve as potential some kinase inhibitors and adenosine agonists [22-25].

Schiff bases are an important class of organic compounds both synthetically and biologically. These compounds show antibacterial, antifungal, anticancer and herbicidal activities [26-29]. Furthermore, it is known that Schiff bases are utilized as starting materials in the synthesis of organic or inorganic compounds for industrial usage. There are many studies on the electrochemical behaviors of Schiff bases (imines) by cyclic voltammetry (CV). Their reduction potentials are dependent on the types of substituent attached to the aromatic ring [30-34], the size of the aromatic groups on either sides of the imine (–C=N–) group [30-32,35] and the amount of intra-molecular hydrogen bonds [36,37].

In this work, Schiff base: methyl 2-((5-chloro -2- hydroxybenzylidene) amino) -6-methyl -4,5,6,7-tetrahydrothieno[2,3-c]pyridine-3-carboxylate was synthesized by the reaction of methyl 2-amino-6-methyl-4,5,6,7-tetrahydrothieno [2,3-c] pyridine-3-carboxylate and 5-chloro-2-hydroxybenzaldehyde. Synthesized compounds were characterized by elemental analysis, NMR (^{1}H and ^{13}C-APT), ATR and X-ray diffraction methods. The electrochemical behavior of Schiff base was evaluated by cyclic voltammetry (CV), controlled potential electrolysis and chronoamperometry (CA) techniques.

EXPERIMENTAL

Elemental analysis was carried out Elementar Vario Cube Pro, Germany. NMR (^{1}H and ^{13}C-APT) spectrum were obtained in $CDCl_3$ on a Bruker Fourier 300 MHz spectrometer. IR spectrum were measured on Nicholet 6700 spectrometer with ATR aparatus. Crystal structure of Schiff base was characterized by using Bruker D8 VENTURE diffractometer. Voltametric measurements were carried out with IVIUM Stat Electrochemical Analyzer.

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*Synthesis of methyl 2-amino-6-methyl-4,5,6,7-tetrahydrothieno[2,3-c]pyridine-3-carboxylate (**1**)*

A mixture of 1-methylpiperidin-4-one(1.13 g, 10 mmol), methyl 2-cyanoacetate (0.99 g, 10 mmol), sulfur (0.32 g, 10 mmol) in absolute ethanol (15 mL) and Et_3N (1.01 mL, 10 mmol) was stirred at room temperature for 6 h (Scheme 1) until TLC showed complete disappearance of the starting materials. The crude product which precipitated at the end of the reaction was separated by filtration [38-40], dried on vacuo and then recrystallized from ethanol. The chemical analysis gave the following results: Yield:78 %, m.p. 208-210 ˚C; Elemental analysis for $C_{10}H_{14}N_2O_2S$: Calc. C, 53.08; H, 6.24; N, 12.38; S, 14.17. Found: C, 52.61; H, 6.02; N, 12.08; S, 13.97. FT-IR (ATR, cm^{-1}); 3399-3282 (NH_2); 2926 (aliph. C-H), 1699 (C=O). ^1H NMR (300 MHz, $CDCl_3$, ppm); δ= 5.99 (br, 2H, $N\underline{H_2}$); 3.80 (s, 3H, $OC\underline{H_3}$); 3.41 (s, 2H, $C\underline{H_2}$); 2.82 (t, 2H, $C\underline{H_2}$); 2.64 (t, 2H $C\underline{H_2}$); 2.47 (s, 3H, $NC\underline{H_3}$). ^{13}C-APT (75 MHz, $CDCl_3$, ppm); δ= 27.26 (C3); 45.44 ($N\underline{C}H_3$); 50.67 ($O\underline{C}H_3$); 52.36 (C4); 53.23 (C5); 114.48 (C7); 130.60 (C6); 162.25 (C=O); 166.33 (C1).

*Synthesis of methyl 2-((5-chloro-2-hydroxybenzylidene)amino)-6-methyl-4,5,6,7-tetrahydrothieno[2,3-c]pyridine-3-carboxylate (**2**)*

To a solution of methyl 2-amino-6-methyl -4,5,6,7- tetrahydrothieno[2,3-c]pyridine-3-carboxy late (2.26 g, 10 mmol) in 20 mL of ethanol, 5-chloro-2-hydroxybenzaldehyde (1.56 g, 10 mmol) was added dropwise with constant stirring. The mixture was refluxed for 4 hours and yellow precipitate was obtained (Scheme 1). Then, the crude product was dissolved in ethanol and single crystals for X-ray diffraction studies were grown by the slow evaporation method. The chemical analysis gave the following results: Yield: 75%, m.p. 208-210 ˚C; Elemental analysis for $C_{17}H_{17}N_2O_3SCl$: Calc. C, 55.96; H, 4.70; N, 7.68; S, 8.79. Found: C, 55.74; H, 4.48; N,7.47; S, 8.62. FT-IR (ATR, cm^{-1}): 3050 (Ar-H); 2943 (aliph. C-H); 1667 (C=O); 1622 (CH=N). ^1H NMR (300 MHz, $CDCl_3$, ppm); δ= 12.88 (s, 1H, Ar-OH); 8.41 (s, 1H, CH=N); 7.15 (m, 2H, Ar-H); 6.79 (d, 1H, Ar-H); 3.88 (s, 3H, OCH_3); 3.41 (s, 2H, CH_2); 2.82 (t, 2H, CH_2); 2.64 (t, 2H CH_2); 2.47 (s, 3H, NCH_3). ^{13}C APT (75 MHz, $CDCl_3$, ppm); δ= 26.77 (C3); 45.49 ($N\underline{C}H_3$); 51.71 ($O\underline{C}H_3$); 52.12 (C4); 53.98 (C5); 119.14 (C10); 119.88 (C8); 123.77 (C12); 124.53 (C2); 129.45 (C7); 130.95 (C13); 133.37 (C11); 134.60 (C6); 153.04 (C1); 157.45 (C9); 159.58 (C=O); 163.34 ($\underline{C}H$=N).

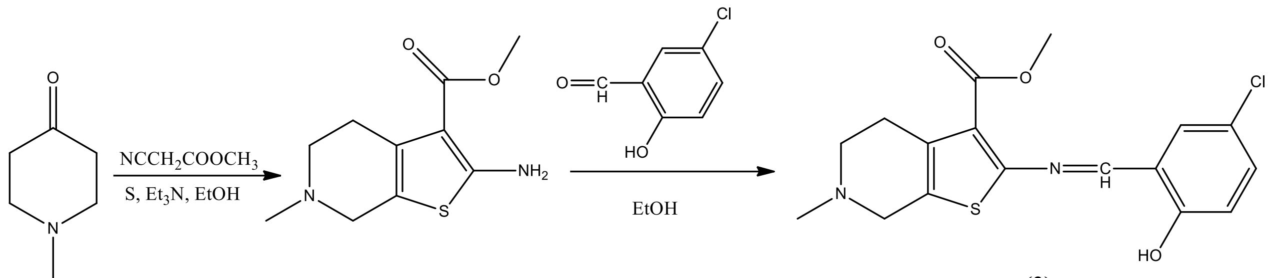
X-Ray crystallography

The rod shaped dark orange single crystal of Schiff base with dimensions 0.05x0.1x0.5mm was grown by slow evaporation of ethanolic solution. Crystal was mounted on a micromount and attached to a goniometer head on a Bruker D8 VENTURE diffractometer equipped with PHOTON100 detector using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) and scanned with 1° Φ-rotation frames at room temperature. Crystal parameters of Schiff base are summarized in Table 1. The structure was solved by intrinsic method SHELXS-1997 [41,42] and refined by using SHELXL-2014/7 (Sheldrick, 2014) [43]. ORTEP drawings with the atomic numbering is given in Fig. 2. and the crystal packing motif is shown in Fig. 3. All the molecular drawings were generated using OLEX2. Ver. 1.2-dev [44]. Thermal ellipsoids were plotted at the 50% probability level. Geometric values for the hydrogen bond are given in Table 2. Selected bond and torsion angles of molecule are given in the Table 3 (CCDC number is 1477724).

Electrochemical studies

In voltammetric measurements, glassy carbon electrode (BAS MF-2012), bulk electrolysis electrode (BAS MF-1056) and 11 µm-ultramicro carbon electrode (BAS MF-2007) were used as a working electrode. A platinum wire was used as the auxiliary electrode (BAS MW-1032). The reference electrode was a silver wire in contact with 0.01 M $AgNO_3$ in dimethylsulfoxide (BAS MF-2052).

The number of electrons transferred (n), the diffusion coefficient (D) and the heterogeneous rate constant (k_s) of Schiff base were determined by ultramicro electrode CV technique of Baranski method and Klingler-Kochi method.



(1)

(2)

Scheme 1. Synthesis method of Schiff base

Table 1. Crystal data for Schiff Base

Empirical formula	$C_{17}H_{17}ClN_2O_3S$(FW. 364.85)
T(K)	300(0)
λ(Å)	0.71073
Crystal system (space group)	Monoclinic(P 1 21/c 1)
Unit cell dimensions: (Å, °)	
a , b, c	11.2530(7), 10.4582(5), 28.7130(16)
V(Å^3)	3379.1(3)
α, β, γ	90, 90.289(2), 90

Table 2. H bonding distances

Donor---Hydrogen...Acceptor	D--H [Å]	H--A [Å]	D--A [Å]	D--H-----A
O6---H13...N4	0.820(4)	1.884(9)	2.606(12)	2.606(12)

Table 3. Selected bond lenghts (Å)

O6	C15	1.3428(1)	C6	C9	1.5030(1)	C16	C14	1.3742(1)
Cl2	C16	1.7428(1)	C9	N3	1.4562(1)	C14	C13	1.4013(1)
N4	C1	1.3743(1)	N3	C10	1.4624(1)	N1	C28	1.4616(1)
N4	C12	1.2813(1)	C15	C17	1.3859(1)	C23	O2	1.2003
C1	S2	1.7421(1)	C17	C18	1.3779(1)	C23	O1	1.3318(1)
S2	C6	1.7225(1)	C18	C16	1.3775	O1	C24	1.4418

Table 4. Selected bond and torsion angles (°)

bond angles (°)				torsion angles (°)				
S2	C1	C2	111.14	N1	C27	C25	C20	-51.8(2)
S2	C6	C5	113.09	C20	C19	S1	C22	1.1(2)
N1	C27	C25	111.03	C21	O2	C23	O1	-179.0(3)
N1	C26	C19	110.28	C22	N2	C29	C30	-175.7(2)
C23	O2	O1	30.18					
C21	C23	O2	123.83					
C23	O1	C24	116.44					
C4	O5	C3	114.52					

Table 5. Reduction peak potentials (E_p^c, V) of Schiff base at different scan rates

0.01 V/s	0.05 V/s	0.1 V/s	0.5 V/s	1 V/s	5 V/s
-1.15	-1.17	-1.19	-1.20	-1.21	-1.28
-2.14	-2.15	-2.17	-2.18	-2.19	-2.21
-2.60	-2.62	-2.64	-2.66	-2.69	-

Table 6. Electrochemical results of Schiff base*

D $(cm^2/s) \times 10^7$ $D \pm ts/\sqrt{N}$	UME Limit current (i. A)$\times 10^{10}$	n (Baranski method)	n (Bulk electrolysis)	k_s $(cm/s) \times 10^4$ $ks \pm ts/\sqrt{N}$
8.85 ± 0.08	2.95 ± 0.02	1.96 ± 0.01	2.01 ± 0.01	9.12 ± 0.05

*Results are average of three measurements and standard deviation.

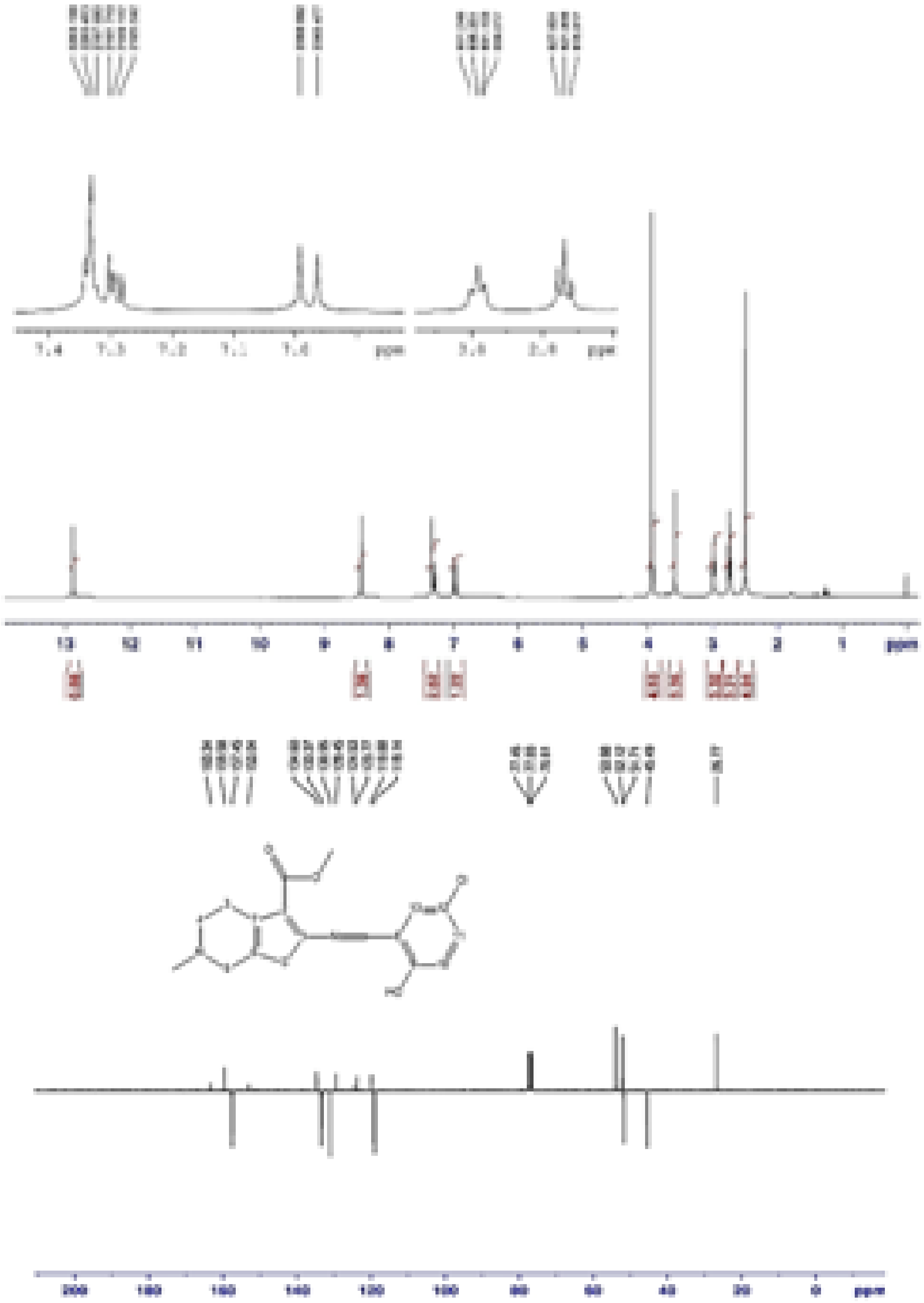


Fig. 1. ^{1}H(left side) and ^{13}C-APT (right side) NMR spectrum of Schiff base.

RESULTS AND DISCUSSION

Structural characterization

^{1}H NMR spectra of methyl 2-((5-chloro-2-hydroxybenzylidene)amino)-6-methyl-4,5,6,7-tetra hydrothieno[2,3-c]pyridine-3-carboxylate shows the following signals in $CDCl_3$ solution. The peak observed at 12.88 ppm is the characteristic of intra-molecular hydrogen bonding of enolic proton (Ar-O$\underline{H}$). The signal of imine (C$\underline{H}$=N) hydrogen is observed at 8.41 ppm [45]. The signal of the aromatic protons are observed at 7.15 ppm and 6.79 ppm, respectively. The signal appearing at 3.88 ppm are corresponds to the methoxy ($OC\underline{H}_3$) protons, the signals at 3.41 ppm, 2.82 ppm and 2.64 ppm are belong to $C\underline{H}_2$ protons of piperidine ring, the signal at 2.47 ppm may be attributed to the methyl group bounded to nitrogen in piperidine. In APT spectra, we observed signals at 26.77 (C3), 52.12 (C4), 53.98 (C5), 119.88 (C8), 123.77 (C12), 124.53 (C2), 129.45 (C7), 134.60 (C6), 153.04 (C1), 159.58 (C=O), 163.34 (CH=N) correspond to positive phases and the signals at 45.49 (NCH_3), 51.71 (OCH_3), 119.14 (C10), 130.95 (C13), 133.37 (C11), 157.45 (C9) correspond to negative phases, respectively. These results is coherent in the literature knowledge. ^{1}H and ^{13}C-APT spectrum of Schiff base are given in Fig. 1.

Crystal structure

According to crystal data (Table 1), -C=N- double bond distance of the imine moiety of 1.281 Å (1) is close to corresponding literature values [46]. The molecule is stabilized by medium strength intra-molecular hydrogen bonding that occurs between hydroxyl proton and imine nitrogen as shown in Fig. 2 and Table 2. The angle between the planes forming thiophene ring and phenyl unit is only 6.57° which shows that two units are nearly on the same plane. The piperidine ring exhibits a slightly distorted chair conformation [47]. Crystal packing of Schiff base is exhibited in Fig. 3, selected bond lenghts (Å), bond and torsion angles (°) are given in Table 3 and 4.

Electrochemical behavior

The electrochemical behavior of Schiff base was evaluated by cyclic voltammetry (CV), controlled potential electrolysis and chronoamperometry (CA) techniques. The cyclic voltammogram of Schiff base was taken at different scan rate (0.01-5 V/s) as seen in Fig.4. Schiff base is also electrochemically active and its reduction potetials (E_p^c) are given in Table 5.

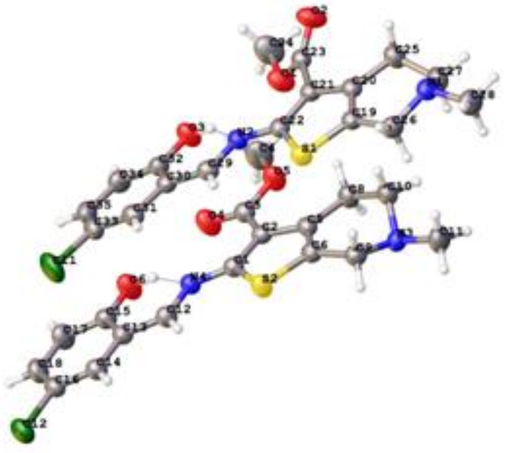


Fig. 2. The labeled diagram of asymmetric unit (intra-molecular hydrogen bonding)

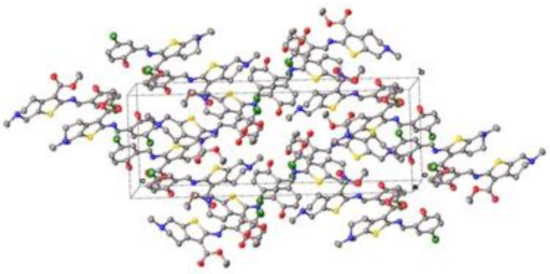


Fig. 3. Crystal packing of Schiff base (hydrogen atoms are omitted for clarity)

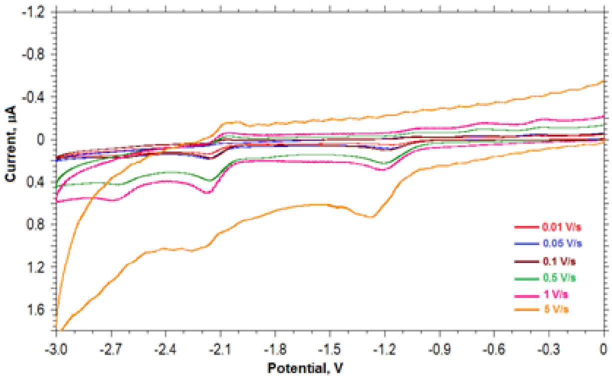


Fig. 4. Cyclic voltamogram of Schiff base in DMSO containing 0.1 M TBATFB on glassy carbon electrode at a scan rate of 0.01 Vs^{-1}(vs. Ag/Ag^{+})

The number of electrons transferred (n) and the diffusion coefficient (D) related with the diffused amount of compound to the electrode surface were determined (Table 6) by using ultramicro electrode and chronoamperometry methods [48-50]. The heterogeneous standard rate constant (k_s) is also found by Klingler-Kochi method (as seen Table 6).

The scan rate, reduction peak potential (E_p^c) and peak width ($E_{p/2}$) affect the value of k_s [51-54].

The electrochemical studies show that the electron transfer follows electrochemical reduction (EC) mechanism. It is supposed that EC mechanism occurs over 2e$^-$ transferring through imine (-CH=N) group. The action mechanism of Schiff base can be useful for pharmacokinetic and pharmacodynamic purposes in biological systems as drugs.

CONCLUSIONS

Schiff base has been synthesized by the reaction of methyl 2-amino-6-methyl-4,5,6,7-tetrahydrothieno [2,3-c]pyridine-3-carboxylate with 5-chloro-2-hydroxybenzaldehyde and characterized by elemental analysis, ATR, ^{1}H and ^{13}C APT methods. Crystal studies show that our molecule has intra-molecular hydrogen bonding between hydroxyl proton and imine nitrogen atoms.

Based on the electrochemical results, the reaction mechanism of Schiff base can conveniently be claimed as electrochemical reduction (EC) mechanism. The number of electrons transferred calculated with the use of UME is in good accordance with the number of electrons determined from bulk electrolysis. The electron transferred follows EC mechanism which contributes to the suggestion of the biochemical behavior of Schiff base.

Acknowledgments: *We thank for financially supported by Hitit University (No. FEF19004.13.001).*

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