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Synthesis, spectroscopic characterization and antibacterial activities of three Schiff bases derived from dehydroacetic acid with various substituted anilines

[Çeşitli substitute anilinler ile birlikte dehidroasetik asitten türetilen üç Schiff bazın sentezi, spektroskopik karakterizasyonu ve antibakteriyal aktiviteleri]*

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ABSTRACT

Objective: Aim and rationale of this study was to synthesize and characterize Schiff bases derived from dehydroacetic acid with various substituted anilines due to their potential antibacterial activities.

Methods: Schiff bases like $C_{15}H_{15}NO_4$ (HL1), $C_{14}H_{11}NO_3Cl_2$ (HL2) and $C_{16}H_{17}NO_3$ (HL3) were synthesized in good yields by the reaction with dehydroacetic acid (DHA) with a number of substituted anilines using the standard methods used in organic synthesis. Their antibacterial activities were investigated against four bacteria, two G (+) i.e. *Staphylococcus aureus, Bacillus subtilis* and two G (-) bacterial strains i.e. *Escherichia coli* and *Pseudomonas aureginosa* by the agar well diffusion method. Synthesized products were characterized by elemental analysis (CHNS), FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy.

Results: The ^{1}H NMR data revealed a strong intramolecular H-bonding between the azomethinic nitrogen and the alcoholic proton of pyran ring. Schiff base (HL2) showed better antibacterial activity when compared with other Schiff bases (HL1 and HL3) against the studied microbes.

Conclusion: These newly reported Schiff bases have potential antibacterial activities against four strains of bacteria like *Staphylococcus aureus, Bacillus subtilis, Escherichia coli* and *Pseudomonas aureginosa*.

Key Words: Schiff base, dehydroacetic acid, anisidine, aniline, antibacterial activity

Conflict of interest: The authors declare that there was no conflict of interest in this work.

ÖZET

Amaç: Çalışmanın amacı ve gerekçesi, çeşitli sübstitüte anilinler ile birlikte dehidroasetik asitten türetilen Şift bazların, potansiyal antibakteriyal aktivitelerine bağlı olarak sentezi ve karakterizasyonudur.

Yöntem: Çalışmada $C_{15}H_{15}NO_4$ (HL1), $C_{14}H_{11}NO_3Cl_2$ (HL2) and $C_{16}H_{17}NO_3$ (HL3) gibi şift bazları standart inorganik sentez metotları kullanılarak, çeşitli sübstitüte anilinler ile birlikte dehidroasetik asit (DHA) reaksiyonlarından yüksek bir verim ile sentezlenmişlerdir. Antibakteriyal aktiviteleri 4 farklı tip bakteriye karşı agar difüzyon metodu kullanılarak araştırılmıştır; iki Gr(+) bakteri, *Staphylococcus aureus, Bacillus subtilis* ve iki Gr (-) bakteri, *Escherichia coli, Pseudomonas aureginosa*. Sentezlenen ürünlerin karakterizasyonu elemental analiz (CHNS), FTIR, ^{1}H NMR ve ^{13}C NMR spektroskopisi ile yapılmıştır.

Bulgular: ^{1}H NMR sonuçları, azometinik nitrojen ve piran halkasının hidroksilik protonu arasında kuvvetli bir molekül içi H-bağı varlığını ortaya çıkarmıştır. Şift baz (HL2)'nin çalışılan bakteri suşlarına karşı, şift bazları (HL1 ve HL3)'e göre daha iyi bir antibakteriyal aktivite gösterdiği bulunmuştur.

Sonuç: Yeni rapor edilen bu şift bazları, *Staphylococcus aureus, Bacillus subtilis, Escherichia coli* ve *Pseudomonas aureginosa* suşlarına karşı potansiyal antibakteriyal aktiviteye sahiptirler.

Anahtar Kelimeler: Şift baz, dehidroasetik asit, anisidin, anilin, antibakteriyal aktivite

Çıkar çatışması: Yazarlar arasında çıkar çatışması bulunmamaktadır.

Introduction

Schiff bases are the privileged ligands and attractive due to their stability and ease by which modified variations can be achieved [1]. This class of ligand is flexible in terms of both size and charge [2]. Schiff base ligands and their metal complexes are omnipresent because of their easy synthesis, wide applications and the convenience of diverse structural modifications [3]. Schiff bases have been reported to be potential anticancer drugs [4]. The azomethine linkage of the Schiff bases is responsible for various antibacterial, antifungal, herbicidal, clinical and analytical activities [5, 6]. Schiff base ligands that contain strong donor sites like phenoxo oxygen atoms and imine nitrogen atoms are brilliant for analytical and biological applications [7, 8].

Dehydroacetic acid (dha = 3-acetyl-4-hydroxy-6-methyl-*2H*-pyran-2-one), and compounds derived from it are very important class of compounds for various organic synthesis [9]. It is a good starting material for the synthesis of different heterocyclic compounds [10]. Dehydroacetic acid (dha) is biologically active compound and studies have shown that it has both antibiotic and antifungal effects [1]. In aqueous solutions, it is a very strong antiseptic agent [11]. The compound is widely used in food technology i.e. used to increase the stability of vitamin C and to protect vegetables during processing of food [12]. It is also used as preservatives in fish sausages [13].

All these reasons and facts [14, 15] motivated us to synthesize and structurally characterize the Schiff bases of dehydroacetic acid (Figure 1) with various substituted anilines (Figures 2-4) and also to check the biological activities of these compounds. Keeping in view the bactericidal and fungicidal properties of dehydroacetic acid [13], it is expected that its Schiff bases would have a high degree of activities. So, in the present study, series of three Schiff bases were synthesized by the reaction with dehydroacetic acid with a number of substituted anilines.

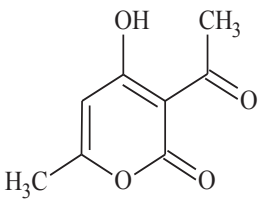


Figure 1. Dehydroacetic acid (3-acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one)

Material and Methods

Reagents and materials

All the reagents used were chemically pure, analytical reagent grade and were used without further purification. The solvents were dried and distilled before use following the standard procedures [16].

Physical measurements

Infrared spectra were recorded with Bio-Rad Excalibure FTIR model 'FTS-3000MX' using KBr pellets in the range 4000-400 cm^{-1}. Melting points were determined with a Mitamura Riken Kogyo, Japan, and were uncorrected. Elemental analysis was performed using a CHN analyzer 'LECO' model CHNS-932. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer in $CDCl_3$ solution at ambient temperature; the $CDCl_3$ signals were used to lock the field and all the chemical shifts (ppm) were assigned relative to tetramethylsilane (TMS); ^{1}H and ^{13}C NMR spectra were measured at 300.132 and 150.90 MHzs respectively.

Preparation of Schiff bases

Synthesis of 4-hydroxy-3-(1-(4-methoxyphenylimino) ethyl)-6methyl-2H-pyran-2-one, C15H15NO4 (HL1)

Dehydroacetic acid (3.36 g, 0.02 mole) was dissolved in dry methanol (35 cm^3). To this 4-methoxy aniline (2.46 g, 0.02 mole) was added and the mixture was refluxed for 1 hour. The resulting black solution was kept at room temperature for several days. Yellow fine crystals of the Schiff base ligand were obtained, washed with methanol and dried in air. Yield: 80% (4.3 g **HL1**). This synthesis of $C_{15}H_{15}NO_4$ (**HL1**) is given in Figure 1.

Synthesis of 3-(1-(2,3-dichlorophenylimino)ethyl)-4-hydroxy-6-methyl-2H-pyran-2-one, $C_{14}H_{11}NO_3Cl_2$ (HL2)

Dehydroacetic acid (3.36 g, 0.02 mole) was dissolved in dry ethanol (50 cm^3). To this 2, 3-dichloroaniline (3.24 g, 0.02 mole) was added and the mixture was refluxed for 1 hour. The resulting solution was kept at room temperature for several days. The solid formed (Schiff base ligand) was filtered and recrystallized from methanol toluene mixture, washed with methanol and dried in air. Yield: 72% (4.6 g **HL2**). This synthesis of $C_{14}H_{11}NO_3Cl_2$ (**HL2**) is given in Figure 2.

Synthesis of 3-(1-(2,3-dimethylphenylimino)ethyl)-4-hydroxy-6-methyl-2H-pyran-2-one, C16H17NO3 (HL3)

Dehydroacetic acid (3.36 g, 0.02 mole) was dissolved in dry ethanol (50 cm^3). To this 2,3-dimethyl aniline (2.50 ml, 0.02 mole) was added and the mixture was refluxed for 30 minutes. The resulting solid was then filtered and re-crystallized from dichloromethane and toluene (3:1) mixture. Yellow fine crystals of the Schiff base ligand werre obtained, washed with methanol and dried in air. Yield: 77% (4.1 g **HL3**). This synthesis of $C_{16}H_{17}NO_3$ (**HL3**) is given in Figure 3.

Antibacterial activity

The antibacterial activities of all the Schiff bases were investigated against four bacteria, two G (+) i.e. *Staphylococcus aureus* (ATCC 25923), *Bacillus subtilis* (DSM

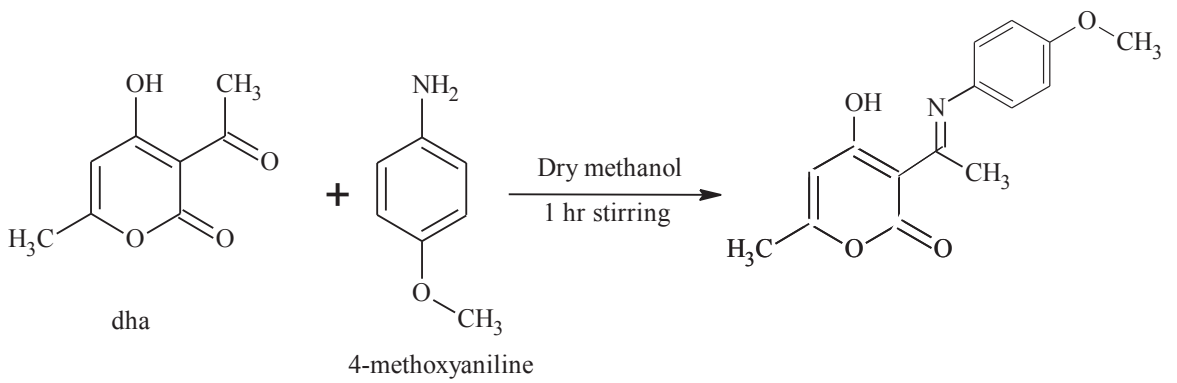


Figure 2. Synthesis of $C_{15}H_{15}NO_4$ (**HL1**)

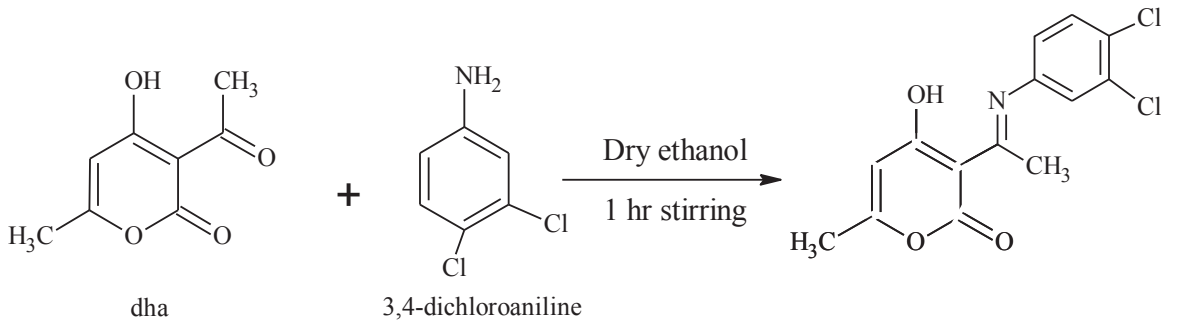


Figure 3. Synthesis of $C_{14}H_{11}NO_3Cl_2$ (**HL2**)

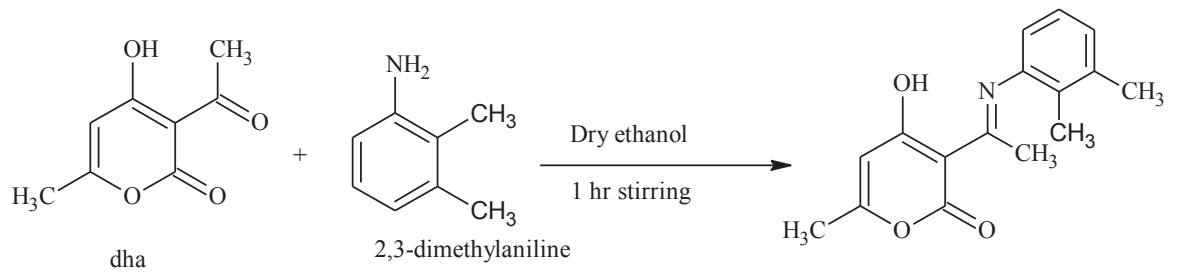


Figure 4. Synthesis of $C_{16}H_{17}NO_3$ (**HL3**)

3256-Germany), and two G (-) bacterial strains i.e. *Escherichia coli* (ATCC 25922), and *Pseudomonas aureginosa* (ATCC 10197) by the agar well diffusion method [6, 7, 14, 15].

Imipenum was used as standard antibiotic drug, which is β-Lactom antibiotic and is effective against G (+) as well as G (-) bacteria. 3 mg of the test sample (Schiff base) was dissolved in 1 mL of DMSO. 2-3 mL nutrient broth (0.8 g / 100 mL) was prepared in distilled water and was autoclaved at 121 °C for 20 minutes with 15 psi pressure. 24 hrs fresh cultures grown on nutrient broth at pH 7 were used for sensitivity testing. To compare the turbidity of bacterial cultures, McFarland $BaSO_4$ solution was used as turbidity standard. To perform antibacterial assay, nutrient agar medium was prepared by dissolving 2g / 100 mL in distilled water and the medium was autoclaved. The nutrient agar medium was poured in Petri plates and allowed to solidify. Using sterile cotton swabs, lawns of test cultures were prepared on labelled plates. Four wells per plate were prepared with the help of sterile cork borer (2 mm). Using micropipette, 30 µL of test solution was poured in respective labelled wells. These experimental plates were incubated for 24 hrs and zones of inhibition (%) were measured. On the average, three readings were taken and compared with standard antibiotic imipenum with inhibition zone of 21, 18, 16, 18 mm respectively.

Results and Discussion

Spectroscopic characterization

Fourier transform infrared spectral data of Schiff base complexes is given in Table 1. The important absorption frequencies are ν(C=O), ν(C-O), ν(OH), and ν(-C=N). In the spectra of the compound **HL2,** a strong band at 3350 cm^{-1} is assigned to enolic proton (–OH) stretching vibration. In compounds **HL1** and **HL3,** no OH bands are observed showing the keto form of the synthesized compound. For ligand **HL1** and **HL3,** IR data suggests the keto form while in ^{1}H NMR data suggests the enolic form of the synthesized compound. A strong band at 1656-1659 cm^{-1} is assigned to azomethine group of Schiff bases. A broad centered band at 3350 cm^{-1} is assigned to –OH stretching vibration along with two deformation bands near 1100 and 1170 cm^{-1}. Also a strong band appears in the range of 1694 cm^{-1} in the free ligand, which is assigned to the C=O group of the pyran ring. The Schiff bases synthesized exist in tautomeric form, mainly as imine-enol form, this is also supported by IR and NMR data [2, 9, 11, 17-19].

Table 1. Fourier transform infrared spectral data of Schiff bases

Schiff base	υ(C=N)	υ(C=O)	υ(C-O)	υ(-OH)
HL1	1655	1697	1326	----
HL2	1659	1693	1358	3350.2
HL3	1655.4	1696.3	1358	----

Analytical data of Schiff base compounds is given in Table 2. Yellow coloured Schiff bases **HL1, HL2** and **HL3**, have the empirical formulas $C_{15}H_{15}NO_4$, $C_{14}H_{11}NO_3Cl_2$, and $C_{16}H_{17}NO_3$ respectively with the uncorrected melting points 170-172, 165-168 and 160-163 ºC respectively. CHN analysis shows that found values for carbon, hydrogen and nitrogen are in good agreement with the calculated ones.

^{1}H NMR data (δ ppm), *J* (Hz) for Schiff bases is given in Table 3. The Schiff base ligands derived from dehydroacetic acid [20] are studied in $CDCl_3$ which indicates that all the ligands exist in tautomeric form. The very down field value of enol ^{1}H NMR indicates a very strong intramolecular hydrogen bonding O-H…N. The resonance stabilization of these compounds favours the enol form [21]. Tan et al. proposed that Schiff bases of dehydroacetic acid primarily exist in keto-amine form [22]. The crystallographic data of DHA-Schiff base with 1, 2-phenylenediamine and 1,3-propylenediamine reported by Cindric et al. also supports the keto-amine form [9]. ^{1}H NMR resonance signal of the protons of methyl group attached to pyran ring appears as a sharp singlet at 1-2 ppm in all the Schiff base ligands. The proton attached to pyran ring at position number 5 appears as a singlet at 5.76 ppm in all the ligands. The methyl groups attached to the azomethine group appears as singlets at 2-3 ppm in all the ligands. The phenyl protons in **HL1**, **HL2** and **HL3** show doublets and multiplets in the range 6.5-7.78 ppm. ^{13}C NMR data (δ ppm), *J* (Hz) for Schiff bases is given in Table 4. The integration of spectra are in good agreement with the composition of the studied compounds.

Antimicrobial studies

Three Schiff bases (**HL1**, **HL2** and **HL3)** are screened in vitro for their microbial activity against four G (+) i.e. single layered structure and G (-) i.e. multilayered human pathogenic bacterial species and the results are summarized in Table 5. These Schiff bases have been found to exhibit considerable activity against *Staphylococcus aureus* and *Bacillus subtilis* (Gram +ve) and *Escherichia coli* and *Pseudomonas aureginosa* (Gram -ve) bacterial species. These bacterial species are also classified due to their differences in the ribosomes of the microbial cells [23]. Blank experiments with standard antibiotic imipenum under identical experimental conditions show 100 % ability to retard the cultured bacterial growth.

The effectiveness of an antimicrobial agent in sensitivity is based on the zones of inhibition [24]. The diameter of the zone is measured to the nearest millimeter (mm). The obtained results indicate that the Schiff bases are also toxic against same microbes under identical experimental conditions. This suggests that the Schiff bases could cross the cell membrane of a microbial cell and enhance their lipophilic characters which subsequently favour its permeation through the lipid layer of the cell membrane. The Schiff bases in this study, retarded microbial activity with small variations against the bacterial species and this difference in activity could be attributed to the impermeability of the cells of the microbes. The observed results seem to conclude that the Schiff base (**HL2**) show better antibacterial activity when compared to other Schiff bases (**HL1** and **HL3**) against the microbes *Staphylococcus aureus, Bacillus subtilis, Escherichia coli* and *Pseudomonas aureginosa*.

Conclusion

Schiff bases were synthesized, tagged as **HL1**, **HL2** and **HL3**, by reacting dehydroacetic acid with several substituted anilines. Schiff bases, with several donor atoms, have potential in analytical applications such as catalysis, numerous enzymatic reactions and in water treatment due to their high complex forming ability with transition metal ions.

The other good pharmaceutical application may be due to their high reactivity against bacteria and fungi that can make them a possible candidate for further antifungal, antibacterial and antibiotic drug.

Conflict of interest: The authors declare that there was no conflict of interest in this work.

Table 2. Analytical data of Schiff bases

Schiff base	Empirical formula	Colour	m. p. (ºC)	Elemental analysis		
				Found (Calculated) %		
				C	H	N
HL1	$C_{15}H_{15}NO_4$	Yellow	170-172	65.93 (64.98)	5.49 (5.63)	5.12 (4.97)
HL2	$C_{14}H_{11}NO_3Cl_2$	Yellow	165-168	53.84 (54.11)	3.52 (3.54)	4.48 (4.67)
HL3	$C_{16}H_{17}NO_3$	Yellow	160-163	70.84 (69.58)	6.27 (6.02)	5.16 (4.99)

Table 3. ^{1}H NMR data (δ ppm), for Schiff bases

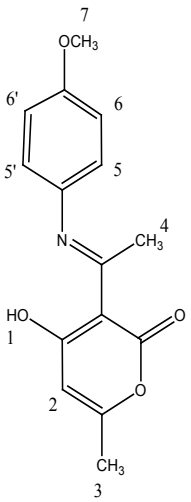
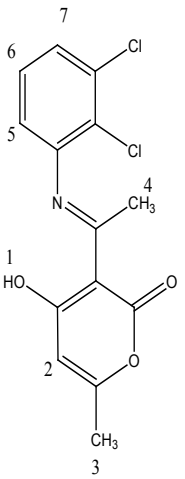
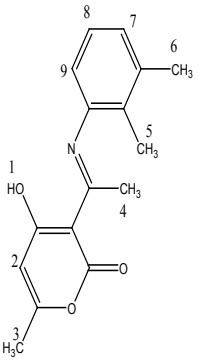
HL1		HL2		HL3	
	H(4) 1.77(s)3H H(3) 2.16(s)3H H(7) 2.60(s)3H H(2) 5.76(s)1H H(1) 15.60(s)1H Aromatic H(5,5') 6.97-6.93 2H Aromatic H(6,6') 7.28-7.07 2H		H(4) 2.18(s)3H H(3) 2.61(s)3H H(2) 5.77(s)1H H(1) 16.00(s)1H Aromatic H(5-7) 7.28-7.55(m)		H(4) 2.16(s)3H H(3) 2.18(s)3H H(6) 2.35(s)3H H(5) 2.49(s)3H H(2) 5.78(s)1H H(1) 15.60(s)1H Aromatic H(7-9) 7.28-6.93(m)3H

Table 4. ^{13}C NMR data (δ ppm), (Hz) for Schiff bases

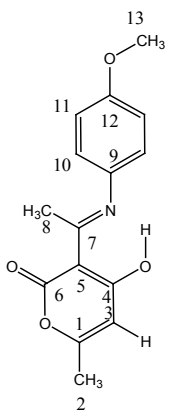
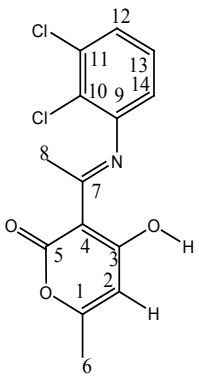
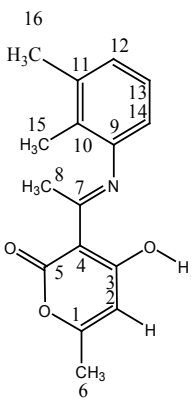
HL1		HL2		HL3	
	C1(163.50) C2(107.25) C3(184.87) C4(97.10) C5(163.20) C6(21) C7(175.54) C8(20) C9(129.06) C10(126.72) C11(115.60) C12(159.50) C13(55.90)		C1(164) C2(106.94) C3(185) C4(97.73) C5(163.07) C6(20.30) C7(175.55) C8(20) C9(135.87) C10(131.27) C11(133.70) C12(127.50) C13(132.27) C14(125.10)		C1(163.60) C2(106.94) C3(185) C4(97.73) C5(163.32) C6(19.94) C7(176.09) C8(14) C9(135.36) C10(138.77) C11(132.43) C12(129.50) C13(126.30) C14(123) C15(14.30) C16(20.13)

Table 5. Antibacterial activities of Schiff bases (zones of inhibition in %)

Compound	G (+) bacteria		G (-) bacteria	
	Staphylococcus aureus (ATCC25923) (%)	*Bacillus subtilis* (DSM3256-Germany) (%)	*Escherichia coli* (ATCC 25922) (%)	*Pseudomonas aureginosa* (ATCC 10197) (%)
Imipenum	100	100	100	100
HL1	00	17±0.14	00	00
HL2	10±0.12	11±0.13	31±0.17	11±0.13
HL3	00	11±0.13	00	6±0.11

References

[1] Iqbal J, Wattoo FH, Tirmizi SA, Wattoo MHS. Dehydroacetic acid oxime as a new ligand for spectrophotometric determination of cobalt. J Chem Soc Pak 2007; 29:136 –139.

[2] Djedouani A, Bendaas A, Boufas S, Allain M, Bouet G, Khan M. Zwitterionic (E)-6-methyl-2-oxo-3-[1-(p-tolyliminio)ethyl]-2H-pyran-4-olate. Acta Cryst 2007; E63: 1271–1273.

[3] Coles SJ, Hursthouse MB, Kelly DG, Toner AJ, Walker NM. Halide titanium(IV) Schiff base complexes; fluoride and bromide derivatives and evidence for a new seven-coordinate chloride intermediate. J Chem Soc, Dalton Trans 1998; 3489–3494.

[4] Aït-Baziz N, Rachedi Y, Silva AMS. Reactivity of some structural analogs of dehydroacetic acid with *o*-phenylenediamine. ARKIVOC 2010; 10: 86–97.

[5] Jarrahpour AA, Motamedifar M, Pakshir K, Hadi N, Zarei M. Synthesis of novel azo Schiff bases and their antibacterial and antifungal activities. Molecules 2004; 9 815–824.

[6] Yang TL, Tai XS, Qin WW, Liu WS, Tan MY. Determination of trace terbium(III) with *N,N′,N″*-tri(3-indolemethanal)triaminotriethylamine: Based on a new fluorescence enhancement system. Anal Sci 2004; 20: 357–361.

[7] Zanello P, Tamburini S, Vigato PA, Mazzochim GA. Syntheses, structure and electrochemical characterization of homo- and heterodinuclear copper complexes with compartmental ligands. Coord Chem Rev 1987; 77: 165–273.

[8] Vigato PA, Tamburini S, Fenton DE. The activation of small molecules by dinuclear complexes of copper and other metals. Coord Chem Rev 1990; 106: 25–170.

[9] Cindric M, Vrdoljak V, Novak TK, C´uric´ M, Brbot-Saranovic A, Kamenar B. Synthesis and characterization of two dehydroacetic acid derivatives and molybdenum(V) complexes: an NMR and crystallographic study. J Molec Struc 2004; 701: 111–118.

[10] Guo Z, Faraglia G, Sitran S. Palladium(II) and platinum(II) complexes with N-substituted methionines. Trans Met Chem 1995; 20: 91–96.

[11] Kubaisi AL, Ismail K. Nickel(II) and palladium(II) chelates of dehydroacetic acid Schiff bases derived from thiosemicarbazide and hydrazinecarbodithioate. Can J Chem 1994; 72: 1785–1788.

[12] Benassi CA, Bettero A, Manzini P, Semenzato A, Traldi P. Interaction between dehydroacetic acid sodium salt and formaldehyde: Structural identification of the product. J Soc Cosmet Chem 1988; 39: 85–92.

[13] Al Alousi AS, Shehata MR, Shoukry MM, Hassan SA, Mahmoud N. Coordination properties of dehydroacetic acid - binary and ternary complexes. J Coord Chem 2008; 61: 1906–1916.

[14] Negm NA, Zaki MF. Structural and biological behaviors of some nonionic Schiff-base amphiphiles and their Cu(II) and Fe(III) metal complexes. Colloid Surface B. Biointerfaces 2008; 64: 179–83.

[15] Chohan ZH, Sumrra SH, Youssoufi MH, Hadda TB. Metal based biologically active compounds: design, synthesis, and antibacterial/antifungal/cytotoxic properties of triazole-derived Schiff bases and their oxovanadium(IV) complexes. Eur J Med Chem 2010; 45: 2739–47.

[16] Perrin DD, Armarego WLF. Purification of laboratory chemicals, 3rd Ed. 1988, Pergamon Press, Oxford, UK.

[17] Luo H, Liu S, Rettig SJ, Orvig C. Rhenium and technetium complexes from pentadentate (N_3O_2) and tetradentate (N_2O_2) Schiff base ligands. Can J Chem 1995; 73: 2272–2281.

[18] Yousef US. A novel conducting polymer film by electrochemical oxidation of 3-[1-(2-aminophenylimino)-ethyl]-6-methylpyran-2,4-dione schiff base in aqueous medium. European Polymer J 2000; 36: 1629–1644.

[19] Cindric M, Novak TK, Uz˘arevic K. Molecular and crystal structures of *N,N*´-propyleneand *N,N*´-phenylene-diylbis[3-(1-aminoethyl)-6-methyl-2H-pyran-2,4(3H)-dione]. J Molec Struc 2005; 750: 135–141.

[20] Chalaca MZ, Figueroa-Villar JD. A theoretical and NMR study of the tautomerism of dehydroacetic acid. J Molec Struct 2000; 554: 225–231.

[21] Manivannan S, Dhanuskodi S. Synthesis, crystal growth, structural and optical properties of an organic NLO material. J Crystal Growth 2004; 262: 473–478.

[22] Tan SF, Ang KP, Jayachandran HL, Jones AJ, Begg WR. ^{1}H, ^{13}C, and ^{15}N nuclear magnetic resonance studies on the tautomerism of the Schiff's bases of 3-acetyl-6-methyl-2*H*-pyran-2,4(3*H*)-dione and 3,5-diacetyltetrahydropyran-2,4,6-trione. J Chem Soc, Perkin Trans-2 1982; 513–521.

[23] Kannan S, Ramesh R. Synthesis, characterization, catalytic oxidation and biological activity of ruthenium(III) Schiff base complexes derived from 3-acetyl-6-methyl-2H-pyran-2,4(3H)-dione. Polyhedron 2006; 25: 3095–3103.

[24] Nath M, Jairath R, Eng G, Song X, Kumar A. Triorganotin(IV) derivatives of umbelliferone (7-hydroxycoumarin) and their adducts with 1,10-phenanthroline: synthesis, structural and biological studies. J Organomet Chem 2005; 690: 134–144.