International Journal of Applied Chemistry.
ISSN 0973-1792 Volume 13, Number 3 (2017) pp. 393-407

http://www.ripublication.com

Synthesis and characterization of some New Oxazepine Compounds Containing 1,3,4-Thiadiazole Ring Derived form D-Erythroascorbic Acid

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Abstract

This search include the synthesis of some new 1,3-oxazepine derivatives have been prepared, starting from reaction of L-ascorbic acid with dry acetone in presence of dry hydrogen chloride afforded the acetal (I). Treatment of the latter with *p*-nitrobenzoyl chloride in dry pyridine yielded the ester (II) which was dissolved in (65%) acetic acid in absolute ethanol yielded the glycol (III). The reaction of the glycol (III) with sodium periodate in distilled water at room temperature produced the aldehyde (IV). The compound (V) [2-amino-5-mercapato-1,3,4-thiadiazole] was prepared through the reaction of thiosemicarbazide with carbon disulphide (CS_2) in entity of anhydrous (Na_2CO_3) in (abs. ethanol). Compound (VI) [2-(5-mercapto-1,3,4-thiadiazol-2-yl)isoindoline-1,3-dione] was synthesized by the reaction of phthalic anhydride with compound (V) in presence of (gla. CH_3COOH). Reaction of compound (VI) with ($ClCH_2COOH$) in entity of anhydrous (Na_2CO_3) in distilled water produced compound (VII) and then reaction with thionyl chloride yielded acid chloride (VIII). Condensation of acid chloride with hydrazine hydrate afforded 2-(5-(1,3-dioxoisoindolin-2-yl)-1,3,4-thiadiazol-2-ylthio)acetohydrazide (IX). The azomethine (X) has been synthesized from the reaction between compounds (IX) and (IV). Moreover compounds (XI-XIII) were synthesized from the cyclic condensation of Schiff base (X) with (maleic, phthalic and 3-nitrophthalic) anhydride, the structures of the novel synthesized compounds have been confirmed by physical properties and spectral measurements such as (FTIR and some of them by ^{1}H-NMR and ^{13}C-NMR).

Keywords: Schiff base, 1,3,4-thiadiazole, 1,3-oxazepine, L-ascorbic acid.

INTRODUCTION

Vitamin C (ascorbic acid), which is a water soluble vitamin used in food and cosmetic industry by change its properties. Vitamin C antioxidant properties because of its ability of quenching or stabilizing free radicals that lead to degenerative diseases, involve cardiovascular, cataracts and cancer[1]. 1,3,4-thiadiazoles are associated with diverse biocidal activities as anticancer, antitubercular, anti-inflammatory, and pesticide agents. These events prompted us to produce compounds that incorporation of amine derivatives would synthesized new compounds with anticonvulsant activity[2].

Imides are the compounds consists of nitrogen atom linked to two carbonyl groups[3]. Imide derivatives are a valuable group of bioactive compounds exhibit androgen receptor antagonists, anti-inflammatory, anxiolytic, antibacterial, and antitumor activity[4]. Schiff bases with the structure (C=N) bond, that formed by condensation of an amine and active carbonyl group[5,6], are the important intermediate for the produce different bioactive compounds as antifungal, antimicrobial, anticancer and antitumor activities[7].

Oxazepines as a "privileged scaffold" are a kind of seven-membered heterocycles with two heteroatoms. They have been studied the molecular properties of this pharmaceutically important nucleus belong to its entity in some natural products and compounds biological active as antithrombotic, antiepileptic, anticonvulsant, anti-inflammatory, antifungal, progesterone agonist, antipsychotic, antagonist and analgesic, antihistaminic, anxiolytics, epidermal growth factor receptor (EGFR) tyrosine kinase inhibitory and antiaggregating activities[8].

EXPERMIENTAL

Melting points were determined by Dig melt MPA 161 (MSRS) electronic and are not corrected. FTIR spectra were recorded on FTIR-600 FTIR spectrometer and 8400s Shimadzu FT infrared spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were carried out by Ultra Shield 300 MHz spectrometer, DMSO-d_6 was used as a solvent with internal standard (TMS), at University of Al al-Bayt, Jordan. TLC was completed on plates of aluminum glaze with strata of (gel of silica), provided via (Merck). The spots have been recognized via (vapor of iodine). whole chemicals have been gained by (BDH and Sigma-Aldrich).

Synthesis of 5,6-*O*-isopropylidene-L-AA (I)[9]

Dry (HCl) was quickly bubble with moving until (20 min) inside a (flask 250ml) including (100ml of dry CH_3COCH_3 & 10g of L-AA). After addition (80ml of C_6H_{14}), moving and refrigeration in an (snow aqueous), decanted has been the supernatant. Washed has been the sediment (4 times) with (154 ml of hexane-acetone) mixture (7:4 v/v), refrigeration in an (snow aqueous) and elimination of supernatant next every addition. The final sediment has been dehydrated beneath miniature pressure to yield (I) (78%) as a white solid, melting point (210-212˚C). R_f (0.68) (methanol: benzene, v/v, 1:1). FTIR (KBr, cm^{-1}): 3244 (O-H), 2993 (C-$H_{ali.}$), 2910 (C-$H_{ace.}$), 1751 (C=$O_{lac.}$), 1660 (C=C), 1435 (C-H_{asym}), 1379 (C-H_{sym}), 1140-900 (C-O), 768 δ(O-H) (O.O.P.)[10].

Synthesis of 2,3-*O*-di(*p*-nitrobenzoyl)-5,6-*O*-isopropylidene-L-AA (II)

(10g, 46mmol) of compound (I) in dry pyridine (50ml) has been cooled, (24g, 129mmol) of (*p*-nitrobenzoyl chloride) was added with moving. The subsequent blend was stirred for (2 hrs), subsequently preserved in murky venue at normal temperature to (22 hrs). Poured has been the mixture inside (ice water) and moving until (20 min), extracted has been the oil layer by (chloroform 2×150 ml), laundered by water, (HCl 5%) (2×100ml), saturated watery $NaHCO_3$ (100ml) & water. Dehydrated over anhydrous $MgSO_4$. Evaporated has been Chloroform. The residue recrystallized from absolute ethanol to give (II) (44%) as a brown solid, melting point (102-104˚C). R_f (0.76) (methanol: benzene, v/v, 1:1,). FTIR (KBr, cm^{-1}): 3078 (C-$H_{ar.}$), 2987 (C-$H_{ali.}$), 2943 (C-$H_{ace.}$), 1745 (C=$O_{lac.}$), 1693 (C=$O_{est.}$), 1606 (C=$C_{ali.}$), 1421 (C=$C_{ar.}$), 1531 ($NO_{2\ asym.}$), 1346 ($NO_{2\ sym.}$), 1263-1105 (C-$O_{est.}$), 900-600 δ(C-H) (O.O.P.)[10].

Synthesis of 2,3-*O*-di(*p*-nitrobenzoyl)-L-AA (III)

(10g, 19.45mmol) of compound (II) was dissolved in blend of (CH_3COOH 65%) (30ml) and (10ml) of (abs. CH_3CH_2OH) and moved until (48 hrs) at normal temperature. The TLC appeared that the interaction has been accomplished (methanol: benzene, 1:1.5). Filter the mixture, (40ml) of a benzene was added to the resulting solution and volatilized (reoccur this procedure four times).

The residue recrystallized from absolute ethanol to yield (III) (74%) as a deep brown solid, m.p (122-124˚C), R_f (0.46) (methanol: benzene, v/v, 1:1.5). FTIR (KBr, cm^{-1}): 3413 (O-H), 3078 (C-$H_{ar.}$), 2985 (C-$H_{ali.}$), 1720 (C=$O_{est.}$), 1603 (C=$C_{ali.}$), 1425 (C=$C_{ar.}$), 1520 ($NO_{2\ asym.}$), 1358 ($NO_{2\ sym.}$), 1275-1105 (C-$O_{est.}$), 900-600 δ(C-$H_{ar.}$) (O.O.P.)[10].

Synthesis of pentulosono-γ-lactone-2,3-enedi(*p*-nitrobenzoate) (IV)

A solution of compound (III) (10g, 21mmol) in (abs. CH_3CH_2OH) (60ml) was added dropwise to the solution of ($NaIO_4$) (5.6g, 26mmol) in distilled water (60ml) at (0˚C) with stirring. (0.5ml) of ($HO\text{-}CH_2CH_2\text{-}OH$) ethylene glycol has been added as dropwise after stirring for (15 min). Stirring was went on at normal temperature for (1 h). (40ml) of distilled water has been added to the mixture after has been filtered subsequently the yield was taken away by (ethyl acetate 3×50ml), the extracts dehydrated via (anhydrous $MgSO_4$), subsequently filtered and the solvent have been removed and recrystallized has been the residue by absolute ethanol to give the compound (IV) (54%) as a yellow solid, melting point (194-196˚C). R_f (0.73) (methanol: benzene, v/v, 1:1.5). FTIR (KBr, cm^{-1}): 3068 (C-$H_{ar.}$), 2993 (C-$H_{ali.}$), 2673, 2548 (C-$H_{ald.}$), 1697 (C=$O_{ald.}$), 1603 (C=$C_{ali.}$), 1423 (C=$C_{ar.}$), 1535 ($NO_{2\ asym.}$), 1356 ($NO_{2\ sym.}$), 1284-1105 (C-$O_{est.}$), 900-600 δ($CH_{ar.}$) (O.O.P.). ^{1}H-NMR (DMSO-d_6 δ ppm): 13.70 (s, 1H, CHO), 8.15-8.34 (dd, 8H, aromatic), 3.92 (s, 1H, lactone ring H-4). ^{13}C-NMR (DMSO-d_6 δ ppm): 178.58 (C=$O_{lac.}$), 165.75 (C=$O_{est.}$), 149.99 (C-3), 123.58-136.32 ($C_{ar.}$), 105.85 (C-2), 47.99 (C-4)[10]. The sign of carbonyl aldehydic has been vanished because of it appeared outside the measure[11].

Synthesis of 2-amino-5-mercapato-1,3,4-thiadiazole (V)[12]

Dissolved of thiosemicarbazide (2g, 21.9mmol) and anhydrous (Na_2CO_3) (2.33g, 21.9mmol) in absolute ethanol (25ml), cooling the solution and (3.2g, 42.1mmol) of CS_2 was added. Heated the resulting mixture under reflux for (7) hours. Cooling the mixture at room temperature. Removed the solvent under low pressure and dissolved the residue in distilled water (20ml), carefully acidified with cold conc. HCl to produce a pale yellow precipitate. Filtered the crude product and rinsed with chilly water, recrystallized from warm water to yield the desired product (V) as yellow needles, yield (69%), m.p. (229-231˚C), lit. (230˚C). FTIR (KBr, cm^{-1}): 3396, 3275 (NH_2), 3097 (N-H) (tautomeric form), 2325 (S-H), 1599, 1535 (C=N), 1496 δ(N-H), 1331 (C-N), 1063 (C=S), 671 (C-S)[10].

Synthesis of 2-(5-mercapto-1,3,4-thiadiazol-2-yl)isoindoline-1,3-dione (VI)[13]

A mixture of equimolar amounts (1mmol) of compound (V) with phthalic anhydride in (15ml) of (gla. CH_3COOH). The mixture was refluxed for (3 hrs). Ice distilled water (25ml) has been added to the medium of reaction and the compound was leaked, dried and recrystallized from absolute ethanol to afford (VI) (54%) as a yellow solid, m.p. (263-265˚C), lit. (266-268˚C). FTIR (KBr, cm^{-1}): 3199 (NH) tautomer, (1734, 1792) ($C=O_{cyclicimide}$), 1603 (C=N), 1547 ($C=C_{ar.}$), 1358 (C-N), 1063 (C=S), 671 (C-S) ^{1}H-NMR (DMSO-d_6 δ ppm): 14.66 (s, 1H, SH), 7.69-8.04 (m, 4H, aromatic), 3.33 (s, 1H, NH tautomer)[10].

Synthesis of 2-(5-(1,3-dioxoisoindolin-2-yl)-1,3,4-thiadiazol-2-ylthio)acetic acid (VII)[14]

(0.15g, 0.57mmol) of compound (7) with (0.12g, 1.1mmol) anhydrous sodium carbonate in (15ml) of distilled water as a solvent were heated, then (0.05g, 0.57mmol) of chloroacetic acid was added. The solution was refluxed for (3) hours. After cooling, acidified the solution by used conc. hydrochloric acid to pH=2. Filtered the product and washed with distilled water and recrystallized from absolute ethanol to award (VII), (56%) as a white solid, m.p. (120-123˚C). FTIR (KBr, cm^{-1}): (3300-2700) (O-H), 3082 ($C-H_{ar.}$), 2897 ($C-H_{ali.}$), 1705 ($C=O_{carboxylic}$), 1576 ($C=C_{ar.}$)[10].

Synthesis of 2-(5-(1,3-dioxoisoindolin-2-yl)-1,3,4-thiadiazol-2-ylthio) acetohydrazide (IX)[15,16]

A mixture of compound (VII) (10mmol) and (4ml) of ($SOCl_2$) in (10ml) of dry benzene was heated for (5 hrs). After chilling the overabundant of ($SOCl_2$) and (benzene) were isolated beneath vacuum. (50mmol) of (hydrazine hydrate 80%) and (dry benzene 15ml) was added to the yield (VIII). The mixture was refluxed for (5 hrs). After cooling, the excess of hydrazine hydrate and solvent were isolated beneath reduce pressure, the residue was washed with ether, then recrystallized from absolute ethanol to give (IX) (77%) as a brown solid, m. p. (170-172˚C). FTIR (KBr, cm^{-1}): 3379 (N-H), (3712, 3167) (NH_2), 3012 ($C-H_{ar.}$), 2966 ($C-H_{ali.}$), 1662 ($C=O_{sec.amide}$), 1604 (C=N), 1558 ($C=C_{ar.}$). ^{1}H-NMR (DMSO-d_6 δ ppm): 11.5 (br. s, 1H, $NH_{sec.amide}$), 7.53-8.07 (m, 4H, aromatic), 3.96 (s, 2H, SCH_2), 3.34 (s, 2H, NH_2)[10].

Synthesis of Schiff base 4-[2-(1,3-dioxo isoindolin-2-yl)-(1,3,4-thiadiazol-2-ylthio)actamido-imine]-pentulose-γ-lactone-2,3-enedi(*p*-nitrobenzoate) (X)

A mixture of 2-(5-(1,3-dioxoisoindolin-2-yl)-1,3,4-thiadiazol-2-ylthio)acetohydrazide (IX) (0.17g, 0.5mmol), aldehyde (IV) (0.2g, 0.5mmol), (10ml) of absolute ethanol and glacial acetic acid 3 drops have been refluxed for (48 hrs). Evaporated the solvent and the residue recrystallized from abs. ethanol to afford (X) (54%) as a deep brown, m.p. (202-204˚C). FTIR (KBr, cm^{-1}): 3417 (N-H), 3032 (C-$H_{ar.}$), 2900 (C-$H_{ali.}$), 1693 (C=$O_{sec.amide}$), 1662 (C=N), 1604 (C=$C_{ali.}$), 1539 (C=$C_{ar.}$), 1523 (NO_2 $_{asym.}$), 1350 (NO_2 sym). ^{1}H-NMR (DMSO-d_6 δ ppm): 8.16-8.35 (dd, 8H, aromatic), 8.08 (d, 1H, CH=N), 7.13-7.91 (m, 4H, aromatic), 4.00 (1H, lactone ring H-4), 3.30 (s, 2H, CH_2). ^{13}C-NMR (DMSO-d_6 δ ppm): 198.87 (C=$O_{lactone\ ring\ and\ cyclicimide}$), 167.32 (C=$O_{sec.amide}$), 165.73 (C-S and C=$O_{ester}$), 160.60 (C-5 and C-N), 149.99 (C-3), 123.26-136.33 ($C_{ar.}$), 72.46 (C-2), 63.02 (C-4), 43.89 (S-CH_2)[10].

Synthesis of 1,3-oxazepines (XI-XIII)

A mixture of equimolar amounts (0.1g, 0.14mmol) of Schiff base (X) and different acid anhydrides such as (maleic, phthalic and 3-nitrophthalic) anhydride (0.14mmol) in (10ml) of dioxane was refluxed for (24 hrs). The solvent was removed and the resulting colored solid recrystallized from absolute ethanol to obtained 1,3-oxazepines (XI-XIII). The nomenclature and physical properties of synthesized compounds are registered in Table (1). The FTIR absorption bands facts are fixed in Table (2).

Table 1: Nomenclature and physical properties of 1,3-oxazepine compounds (XI-XIII)

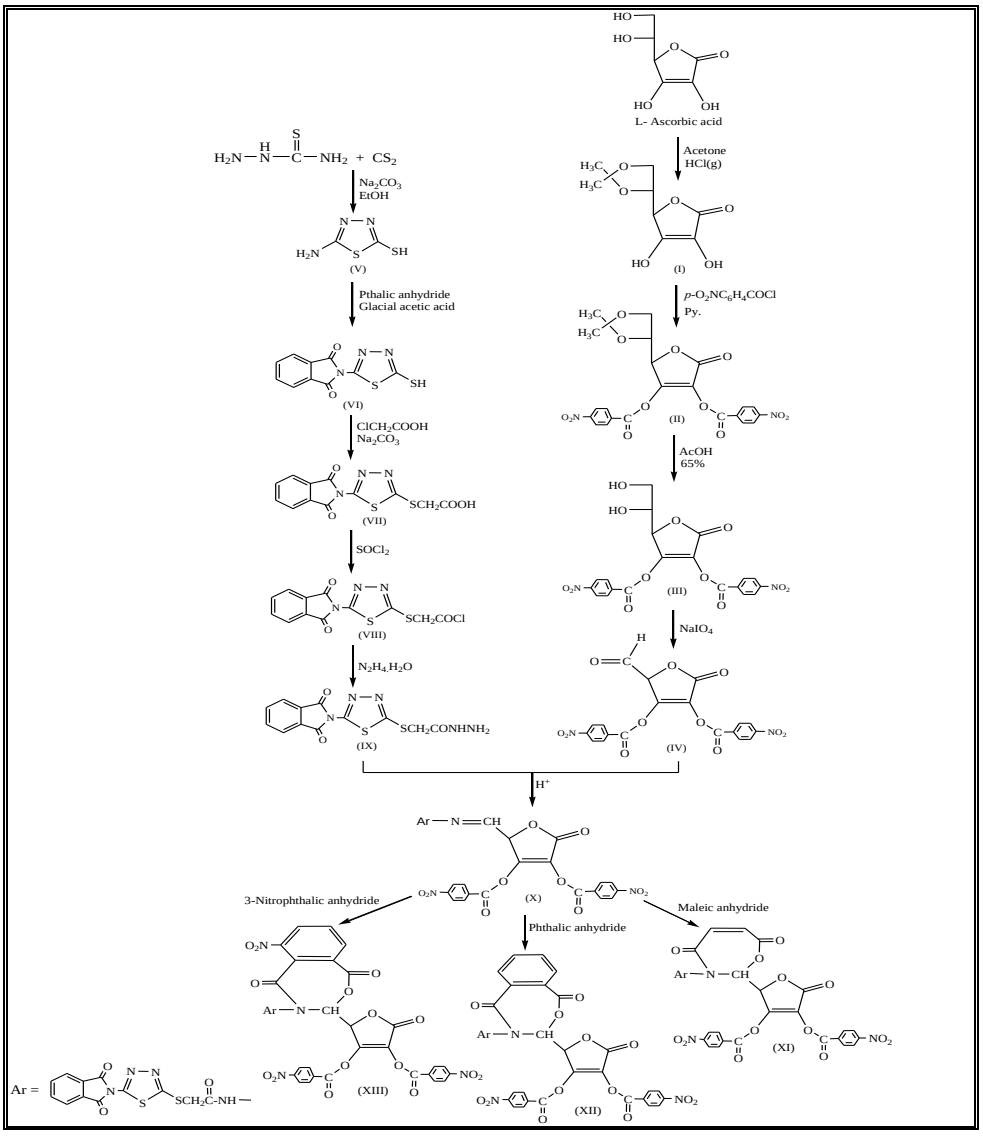
Comp. No.	Nomenclature	Molecular formula	M.p. ˚C	Color	Yield %
XI	2-(pentulose-γ-lactone-2,3-enedi(*p*-nitrobenzoate)-3-[2-(1,3-dioxoisoindolin-2-yl)-(1,3,4-thiadiazol-2-ylthio)actamide]-2,3-dihydro-[1,3]-oxazepine-4,7-dione	$C_{35}H_{19}O_{16}N_7S_2$	244-246	Pale brown	64
XII	2-(pentulose-γ-lactone-2,3-enedi(*p*-nitrobenzoate)-3-[2-(1,3-dioxoisoindolin-2-yl)-(1,3,4-thiadiazol-2-ylthio)actamide]-2,3-dihydrobenz[1,2e][1,3]-oxazepine-4,7-dione	$C_{39}H_{21}O_{16}N_7S_2$	232-234	Pale brown	75
XIII	2-(pentulose-γ-lactone-2,3-enedi(*p*-nitrobenzoate)-3-[2-(1,3-dioxoisoindolin-2-yl)-(1,3,4-thiadiazol-2-ylthio)actamide]-2,3-dihydro(3-nitrobenz)[1,2e][1,3]-oxazepine-4,7-dione	$C_{39}H_{20}O_{18}N_8S_2$	176-178	Yellow	77

Table 2: The FTIR absorption bands data of 1,3-oxazepine compounds (XI-XIII)

Comp. No.	N-H	C-H ar.	C-H ali.	C=O lactone	C=O lactam	C=C ali.	C=C ar.	C-O-C est.	NO_2 asym.	NO_2 sym.
XI	3109	3066	2954	1701	1650	1606	1425	1300-1109	1527	1342
XII	3113	3062	2893	1697	1650	1606	1493	1304-1115	1539	1342
XIII	3408	3030	2916	1705	1666	1603	1462	1284-1109	1527	1340

RESULTS AND DISCUSSION

The aim of this work is synthesis of some new 1,3-oxazepine compounds derived from D-erythroascorbic acid, scheme (1).



Scheme 1: The scheme of prepared compounds

To obtain these compounds starting to prepare the acetal (I) from reaction of L-ascorbic acid with dry acetone in presence of HCl gas, following Salomon method[9], then esterification of (OH) groups at positions C-2 and C-3 for compound (I) by used *p*-nitrobenzoyl chloride in presence of dry pyridine yielded compound (II). The structure of compounds (I) and (II) were identified by FTIR spectroscopy. The FTIR spectrum of the ester (II) showed disappearance of absorption band belong to (O-H) at (3244 cm^{-1}) for compound (I) and emergence of absorption band at (1693 cm^{-1}) assigned to (C=O) group of ester for compound (II).

Afforded to the glycol (III) from compound (II) by using (65%) acetic acid with absolute ethanol, the stirring until (48 hrs) at normal temperature. The structure of the glycol (III) was confirmed by FTIR spectrum which was shown appearance of absorption band at (3413 cm^{-1}) due to hydroxyl groups. Oxidation of the glycol (III) by sodium periodate yielded the aldehyde (IV), the FTIR spectrum of compound (IV), Figure (1) showed the absorption band at (1697 cm^{-1}) assigned to (C=O) aldehydic. This compound (IV) appeared a positive Tolen's experiment by forming a mirror of silver [17]. The structure of (IV) was proven by ^{1}H-NMR spectrum, whom offered a signal at δ(13.70) ppm to proton of (H-C=O), Figure (2) and has been identified via ^{13}C-NMR spectrum, Figure (3).

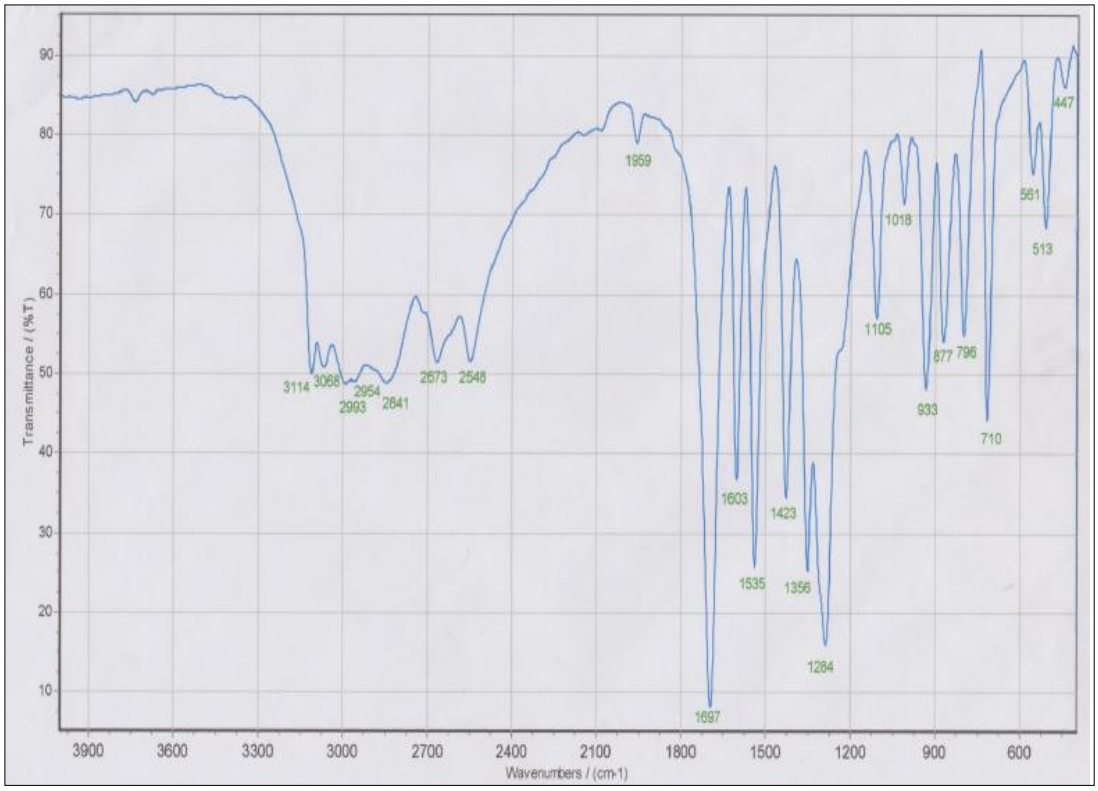


Figure 1: FTIR spectrum of aldehyde (IV)

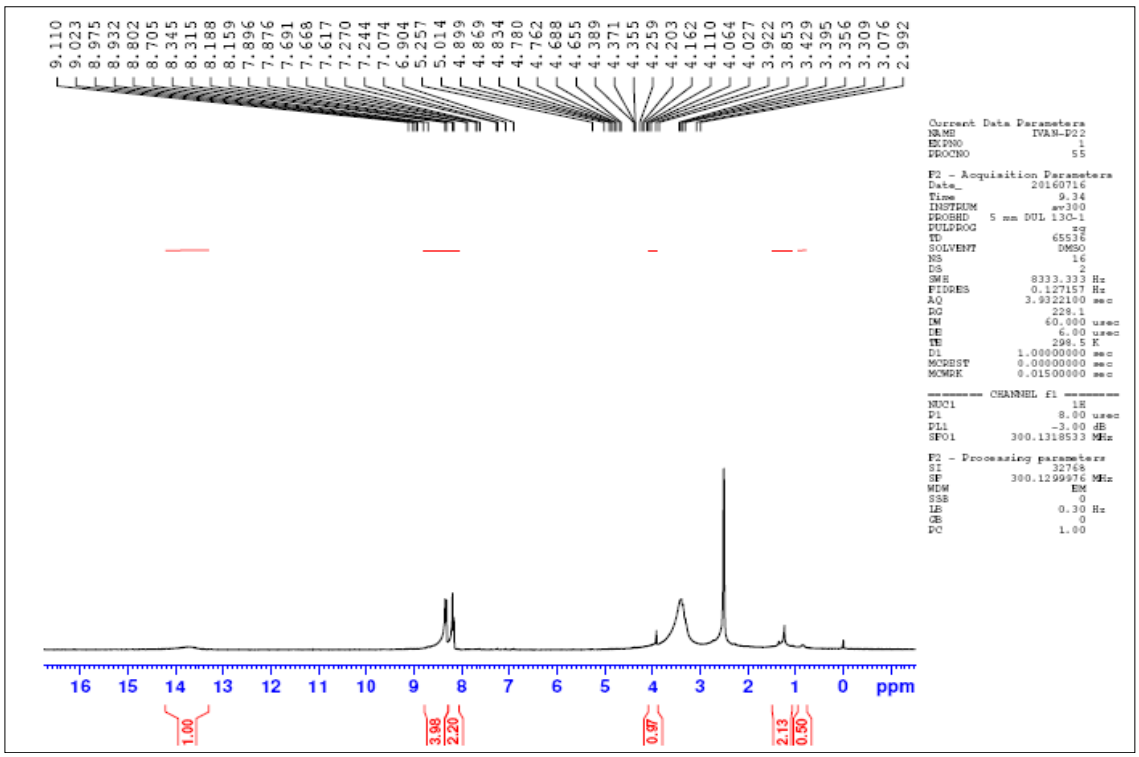


Figure 2: ^{1}H-NMR spectrum of aldehyde (IV)

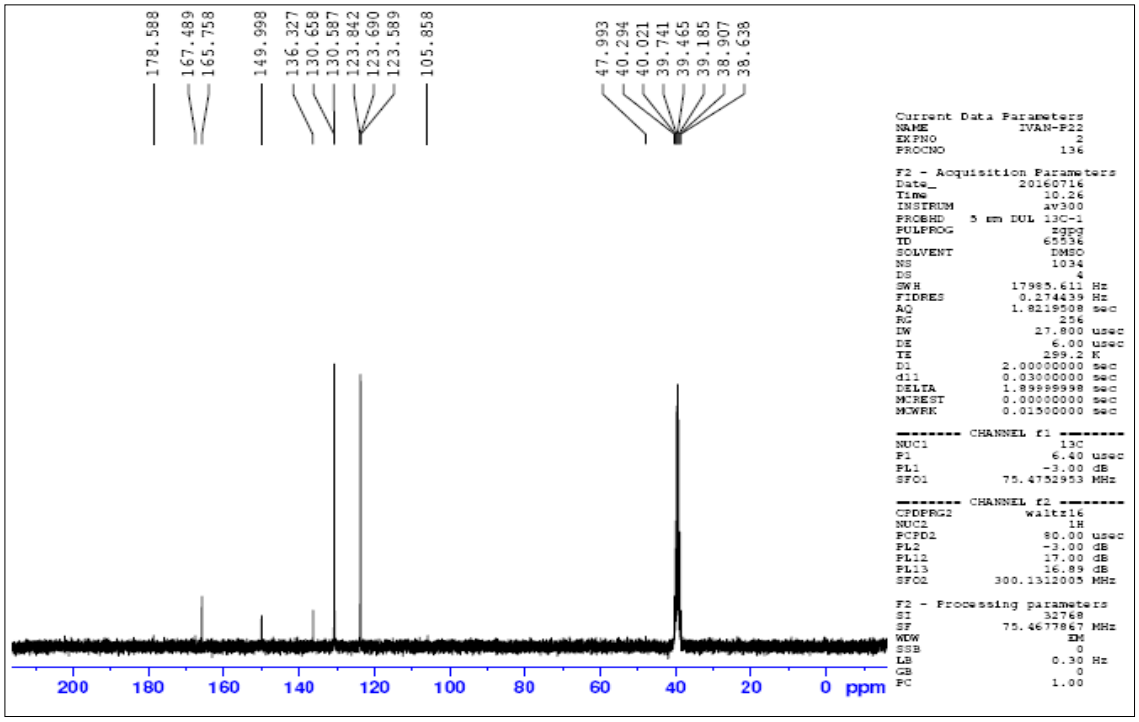


Figure 3: ^{13}C-NMR spectrum of aldehyde (IV)

To prepared the amide (IX), we needed compound (V), which was prepared from reaction of thiosemicarbazide with (CS_2) in presence of anhydrous (Na_2CO_3) in abs. ethanol as a solvent, then converted to compound (VI) by its reaction of phthalic anhydride in glacial acetic acid. The structure of compounds (V) and (VI) were identified by FTIR spectrum and ^{1}H-NMR spectrum for compound (VI). The FTIR spectrum of compound (V) exhibited the absorption bands at (3396, 3275) cm^{-1} assigned to asymmetric and symmetric stretching vibration of (NH_2) and at (2325) cm^{-1} for (SH). The FTIR spectrum for compound (VI) showed disappearance of absorption bands at (3396, 3275) cm^{-1} for (NH_2) and appearance of absorption bands at (1734, 1792) cm^{-1} belong to (C=O) of cyclicimide. The ^{1}H-NMR spectrum for compound (VI) showed the following signals: singlet peak at δ(3.33) ppm for (1H, NH tautomer), multiplet peaks at δ(7.69-8.04) ppm due to aromatic protons and singlet peak at δ(14.66) ppm for (1H, SH).

Reaction of compound (VI) with ($ClCH_2COOH$) in existence of anhydrous (Na_2CO_3) in distilled water as a solvent yielded compound (VII), which was characterized by FTIR spectrum. The FTIR spectrum of compound (VII) demonstrated emergence of band at (1705) cm^{-1} for carboxylic group. Compound (VII) was converted to acid chloride by its reaction of thionyl chloride to produced compound (VIII). Finally, to obtain amide (IX) by reaction of acid chloride with hydrazine hydrate in benzene. The structure of amide (IX) was identified by FTIR and ^{1}H-NMR spectra. The FTIR spectrum of compound (IX), Figure (4) exhibited the absorption bands at (3379, 3271, 3167) cm^{-1} assigned to (NH) and asymmetric and symmetric stretching vibration of (NH_2), in addition to the absorption bands at (1662 and 1604) cm^{-1} due to (C=O) sec. amide and (C=N). The ^{1}H-NMR spectrum for compound (IX), Figure (5) showed the following signals: singlet peak at δ(11.5) ppm for (1H, NH sec. amide), multiplet peaks at δ(7.53-8.07) ppm due to aromatic protons, singlet peak at δ(3.96) ppm for (2H, SCH_2) and singlet peak at δ(3.34) ppm for (2H, NH_2).

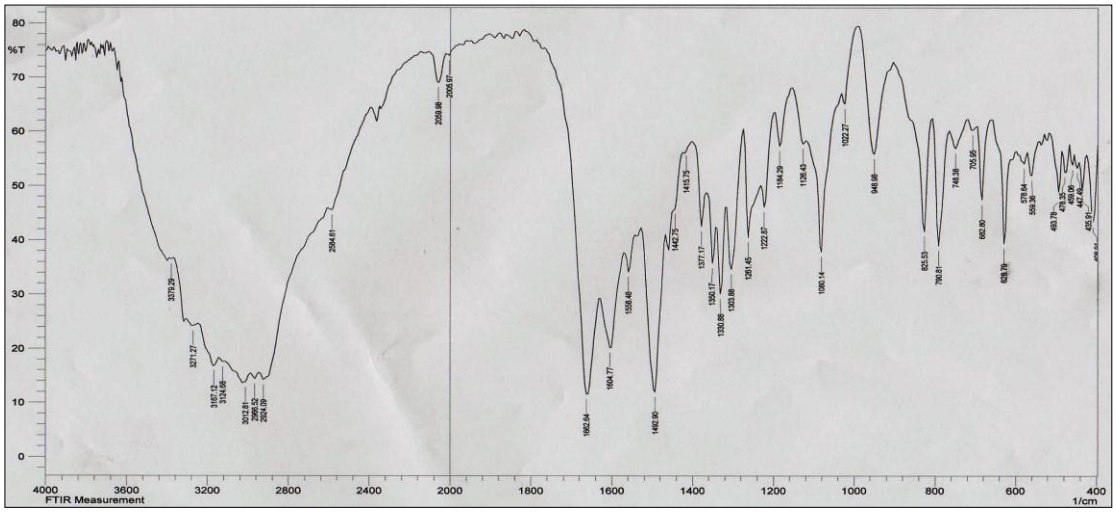


Figure 4: FTIR spectrum of amide (IX)

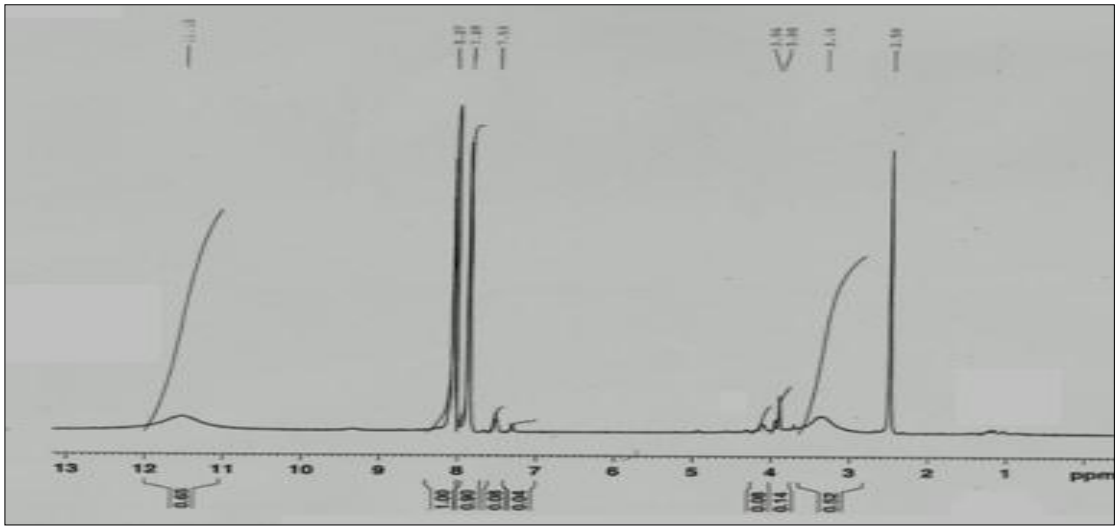


Figure 5: ^{1}H-NMR spectrum of amide (IX)

Schiff base (X) was synthesized by condensation reaction of aldehyde (IV) with amide (IX) and few drops of glacial acetic acid in presence of absolute ethanol as a solvent. The structure of Schiff base was characterized by FTIR, ^{1}H-NMR & ^{13}C-NMR spectra. The FTIR spectrum of Schiff base, Figure (6) revealed vanishing of bands at (3271, 3167) cm^{-1} assigned to (NH_2) for amide (IX) and band at (1697) cm^{-1} due to (C=O) for aldehyde (VI) and appearance of absorption band at (1662) cm^{-1} for (C=N). The ^{1}H-NMR and ^{13}C-NMR spectra for Schiff base (VII), Figures (7) and (8) showed the following signals: 8.16-8.35 (dd, 8H, aromatic), 8.08 (d, 1H, CH=N), 7.13-7.91 (m, 4H, aromatic), 4.00 (1H, lactone ring H-4), 3.30 (s, 2H, CH_2), 198.87 (C=O lactone ring and cyclicimide), 167.32 (C=O sec. amide), 165.73 (C-S and C=O ester), 160.60 (C-5 and C-N), 149.99 (C-3), 123.26-136.33 (C aromatic), 72.46 (C-2), 63.02 (C-4), 43.89 (S-CH_2).

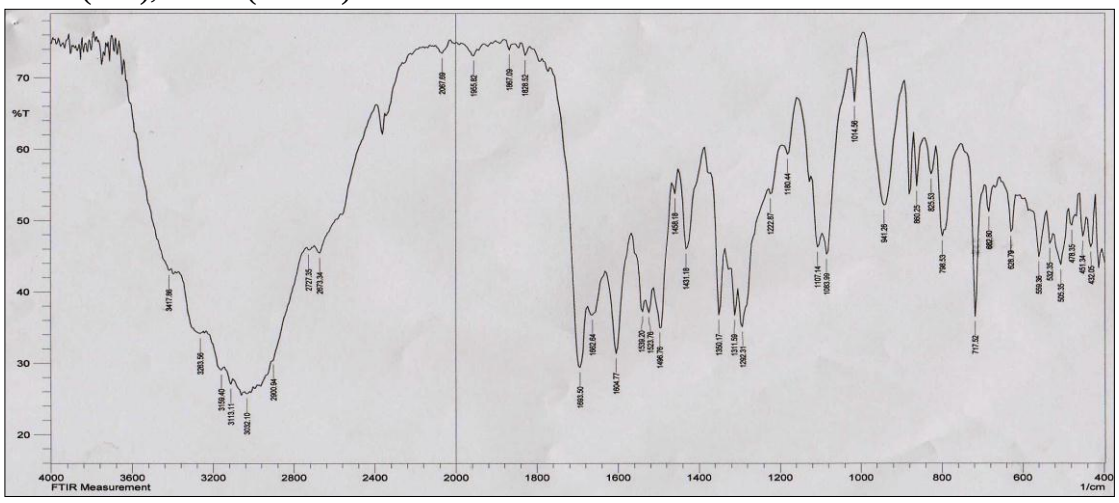


Figure 6: FTIR spectrum of Schiff base (X)

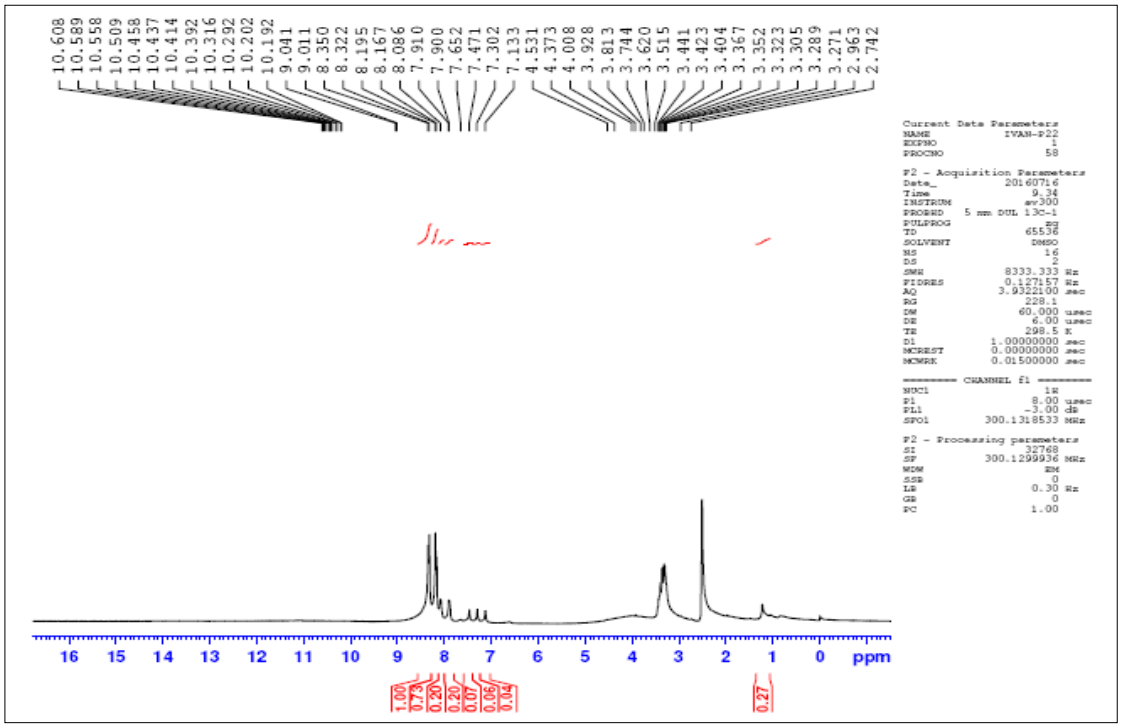


Figure 7: ^{1}H-NMR spectrum of Schiff base (X)

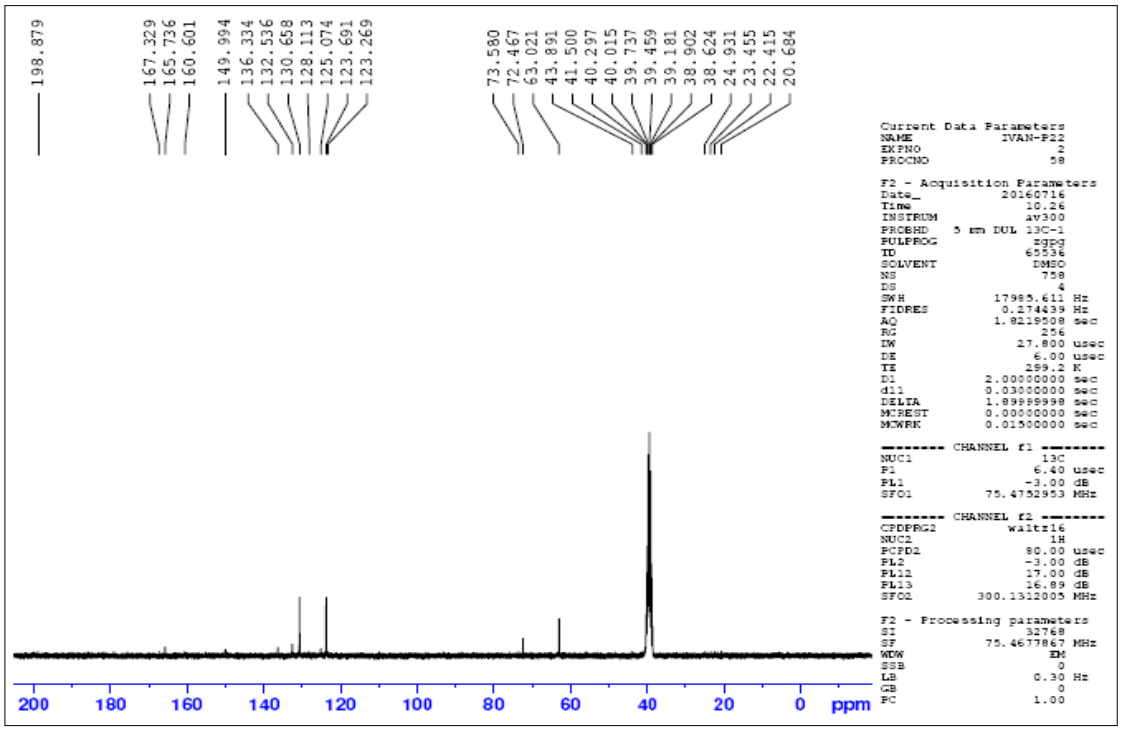
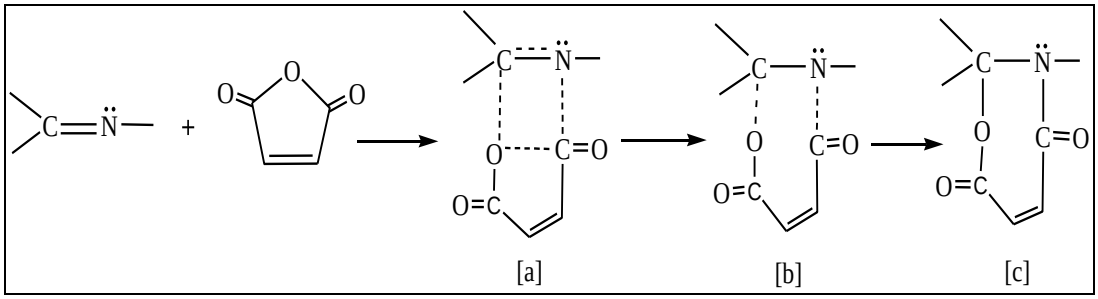


Figure 8: ^{13}C-NMR spectrum of Schiff base (X)

Finally, 1,3-oxazepine compounds (XI-XIII) were synthesized from 1,3-dipolar cycloaddition reaction of Schiff base (X) with different acid anhydrides such as (maleic, phthalic and 3-nitrophthalic) anhydride in dioxane as a solvent. The mechanism of the reaction is shown in scheme (2).



Scheme 2: The mechanism of formation of 1,3-oxazepine

The mechanism involves the addition of one σ-carbonyl to π-bond (N=C) to give 4-membered cyclic and 5-membered cyclic ring of anhydride in the same transition state $[T.S.]_a$, which opens into (maleic, phthalic and 3-nitrophthalic) anhydride to give 7-membered cyclic ring 1,3-oxazepine [C][18]. The FTIR spectra indicated bands at (1697-1705) cm^{-1} for lactone and (1650-1666) cm^{-1} for lactam and evanescence of absorption band at (1662) cm^{-1} to (C=N) of Schiff base (X), FTIR spectrum for compound (XIII), Figure (9). The ^{1}H-NMR and ^{13}C-NMR spectra for compound (XIII), Figures (10) and (11) showed the following signals: 8.16-8.34 (dd, 8H, aromatic), 7.69-8.12 (m, 7H, aromatic), 6.02 (1H, H-5), 5.28 (1H, lactone ring H-4), 3.40 (s, 2H, CH_2), 165.99 (C=O sec. amide and lactam), 165.86 (C=O lactone ring and cyclicimide), 165.78 (C=O ester and C-S), 149.98 (C-3), 123.69-136.45 (C aromatic), 86.85 (C-2), 77.45 (C-5), 63.03 (C-4), 44.60 (S-CH_2).

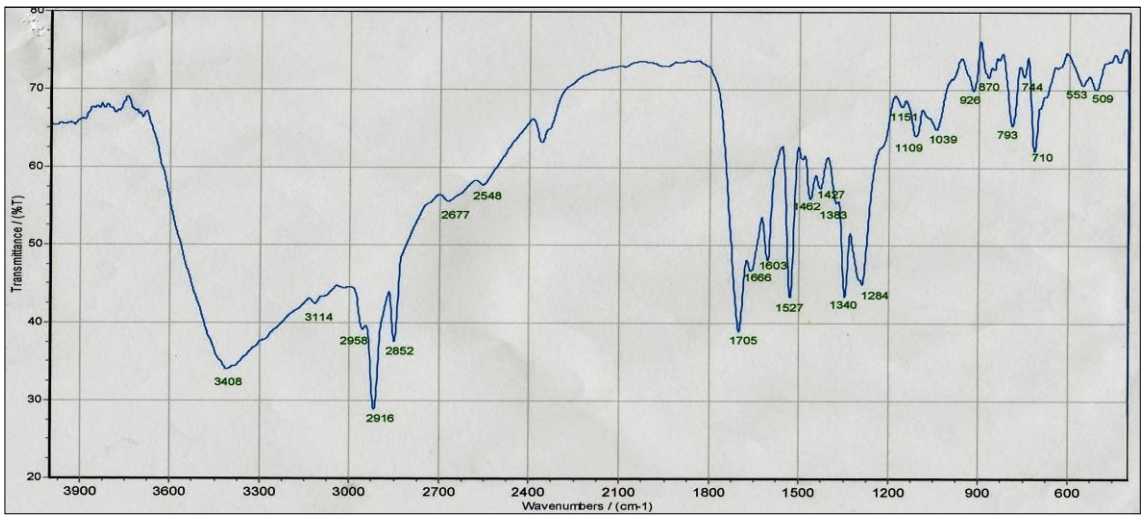


Figure 9: FTIR spectrum of compound (XIII)

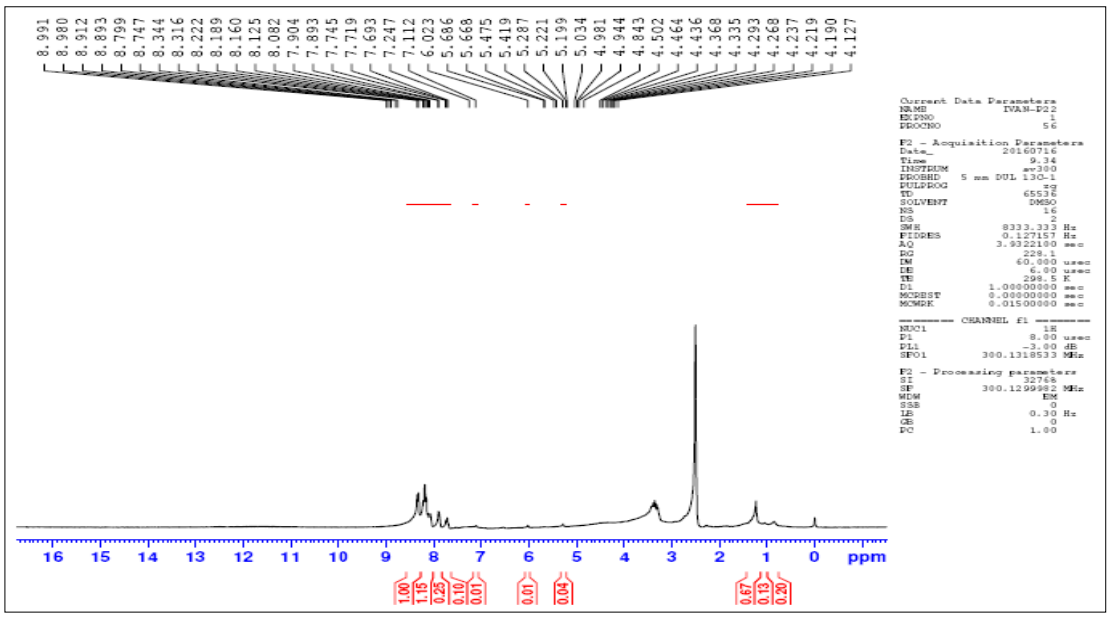


Figure 10: ^{1}H-NMR spectrum of compound (XIII)

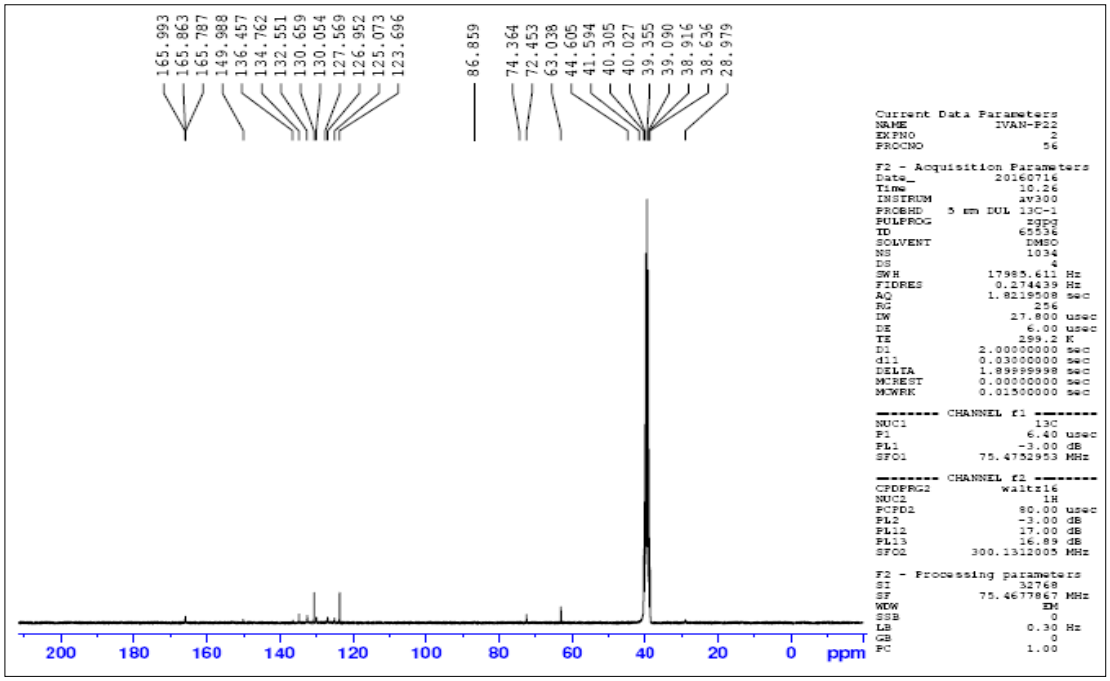


Figure 11: ^{13}C-NMR spectrum of compound (XIII)

CONCLUSION

We prepared the new compounds objective of the study and was to prove their structures by Fourier transform infrared spectroscopy and some of them via ^{1}H-NMR and ^{13}CNMR spectra.

REFERENCES

[1] Marcela, F., Lucía, C., Esther, F., and Elena, M., 2016, "Microencapsulation of L-ascorbic acid by spray drying using sodium alginate as wall material", Journal of Encapsulation and Adsorption Sciences, 6, 1-8.

[2] Rahman, M.A., Shakya, A.K., Wahab, S., and Ansari, N.H., 2014, "Synthesis of some new thiadiazole derivatives and their anticonvulsant activity", Bulgarian Chemical Communications, 46(4), 750- 756.

[3] Sharma, S., Jain, A.D.K., Aggarwal, A., and Gill, N.S., 2012, **"**Synthesis, characterization and pharmacological evaluation of novel Schiff bases of imide moiety", J. Med. Sci., 12(3), 61-69.

[4] Abdel-Aziz, A.A.-M., 2007, "Novel and versatile methodology for synthesis of cyclic imides and evaluation of their cytotoxic, DNA binding, apoptotic inducing activities and molecular modeling study", European Journal of Medicinal Chemistry 42, 614-626.

[5] Khouba, Z., Benabdallah, T., and Maschke, U., 2009, "Spectrophotometric study of liquid crystals containing pentadentate Schiff base type systems, Physics Procedia, 2, 1305-1311.

[6] Zhang, L.X., Liu, Y., Cia, L.H., Hu, Y.J., Yin, J., and Hu, P.Z., 2006, "Inhibitory study of some novel Schiff base derivatives on *staphylococcus aureus* by microcalorimetry", Thermochimica Acta, 440, 51-56.

[7] Kailas, K., Sheetal, J., Anita, P., and Apoorva, H., 2016, "Four synthesis methods of Schiff base ligands and preparation of their metal complex with IR and antimicrobial investigation", World Journal of Pharmacy and Pharmaceutical Sciences, 5(2), 1055-1063.

[8] Hajishaabanha, F., and Shaabani, A., 2014, "Synthesis of oxazepin-quinoxaline bis-heterocyclic scaffolds via an efficient three component synthetic protocol, The Royal Society of Chemistry, 4, 46844–46850.

[9] Salomon, L.L., 1963, "Preparation of 5,6-O-isopropylidene-L-ascorbic acid"; Experientia 19(12), 619-620.

[10] Dudley, H., and Fleming, I., 1995, "Spectroscopic Methods in Organic Chemistry", 5th Ed., McGraw-Hill companies, London; Vol. 24.

[11] Carey, F.A., 2006, "Organic Chemistry"; 6th Ed., the McGraw-Hill Companies, Inc., New York; pp. 767.

[12] Salih, N.A., Ph. D. Thesis, College of Science, Al-Nahrain University, Iraq, 2005.

[13] Hasan, S.M., Samir, A.H., and Majeed, I.Y., 2014, "Synthesis and characterization of novel Schiff bases of imide moiety", Ibn Al-Haitham J. for Pure and Applied Science, 27(3), 407-420.

[14] Sharba, A.H., Hassan, H.A, and Hassan, D.F., 2012, "Synthesis of heterocyclic compounds derived from 2-mercapto quinoline", Ibn Al-Haitham .J. for Pure and Applied Science, 25(3), 242-252.

[15] Said, F.M., Al-Bayati, R.I., and Al-Juboori, A., 2006, "Synthesis of some substituted 1,3,4-thiadiazoles", Al-Mustansiriya J. Sci, 17(3), 15-26.

[16] Bayrak, H., Demirbas, A., Karaoglu, S.A., and Demirbas, N., 2009, "Synthesis of some new 1,2,4-triazoles, their Mannich and Schiff bases and evaluation of their antimicrobial activities", European J. of Med. Chem., 44(3), 1057-1066.

[17] Vogel, A.I., 1989, "Vogel's Textbook of Practical Organic Chemistry"; 5th Ed., John Wiley and Sons, Inc., New York; pp. 1219.

[18] Tawfig, M.T., Ph. D. Thesis, College of Education-Ibn-Al-Haitham, Baghdad University , Iraq, 2004.