

Synthesis and characterization some of α,β -unsaturated aliphatic ketones derivatives

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Abstract :-

Starting compound 4-(furan-2-yl)-but-3-en-2-one(aliphatic ketone) has been prepared by treating furfuraldehyde with acetone, which reacted with diethylmalate to give diketo ester(1), then converted (1) to corresponding pyrazole derivative(2) by reacted with (2, 4-dinitro phenyl hydrazine). Pyrazole derivative (2) reaction with hydrazine hydrate to gives acid hydrazide (3), then reaction of (3) with aldehydes (benzaldehyde) to yield Schiff base (4) and with ketones (acetophenone) to yield Schiff base (5). Schiff base (4) converted into oxadiazole cyclic (6) by reacted with acetic anhydride.

INTRODUCTION:-

α,β -unsaturated aliphatic ketones, structures are double bonded is adjacent to the carbonyl group, have been used as starting materials for the synthesis of various chemicals, including plastics, resins, pesticides, dyes, and pharmaceuticals. They are also found in naturally occurring compounds such as plant allelochemicals, and insect hormones and pheromones ⁽¹⁾. There has been a considerable interest in the chemotherapeutic activity of pyrazole derivatives as they are reported to exhibit broad spectrum biological effects⁽²⁾. Furthermore many substituted oxadiazoles⁽³⁾, thiadiazoles⁽⁴⁾ and thiotriazoles⁽⁵⁾ have wide range of pharmacological and therapeutic activities in addition to have hypoglycemic effect. These facts encouraged the idea of incorporation of a pyrazole ring with an oxadiazole ring which might result in potential biologically active agents ⁽⁶⁾.

Keywords: *p*-dimethylaminobenzaldehyde; *P*-anisaldehyde; Schiff base; mesalazine

EXPERIMENTAL PART INSTRUMENTS

- 1- Melting points were determined by using Melting Point SMP3 apparatus.
- 2- F.T.I.R. spectra were recorded by using Fourier Transform Infrared Spectrophotometer (F.T.I.R) 8400 S Shimadzu apparatus.
- 3- U.V. spectra were recorded by using U.V-Visible Spectrophotometer 1650 PC Shimadzu apparatus.

SYNTHETIC METHODS:-

Synthesis of starting material (α,β -unsaturated aliphatic ketone) (4-(furan-2-yl) but-3-en-2-one) ⁽⁷⁾

A mixture of (65ml) of redistilled furfural and (600ml) of water was put in a litre bolt-heat flask, equipped with a mechanical stirrer then added (120ml) of acetone. Stirring the mixture and cooled to 10°, then added to a solution of (5gm) of sodium hydroxide in (10ml) of water. Continue the stirring without cooling for 4hr. Then added 10 percent sulphuric acid until the mixture is acid to litmus the liquid separated into layers. Separate the lower organic layer and dry it with a little of a hydrous magnesium sulphate and distilled under reduced pressure. Collect the furfural acetone at 114-118°.

The purity of compounds prepared was examined by using the thin layer Kromotografea. R_f values of these compounds were measured using eluent (acetic acid: ethanol: water) 2:4:4 respectively by using silica gel on glass plates.

Ethyl -8-(furan-2-yl)-4, 6-dioxoocta-2, 7-dienoate ⁽⁶⁾ (1)

The appropriate chalcone (15gm) and diethylmalate (10gm) were added to ice-cold suspension of sodium ethoxide (4gm) in dry ether (100ml). The mixture was kept overnight at room temperature and the sodium salt was separated and acidified with 10% H₂SO₄. The resulting ester was recrystallized from ethanol to yield (1).

Ethyl-3-{1-(2,4-dinitrophenyl)-5-[2-(furan-2-yl)ethenyl] -2,3-dihydro-1H-pyrazol-3-yl}prop-2-enoate ⁽⁸⁾ (2)

Solution of ethyl octanoate (1) (0.01mole) in ethanol (20ml) was refluxed with 2, 4-dinitrophenylhydrazine (0.01mole) for 2hr. concentrated and cooled. The result was filtered recrystallized from ethanol to yield (2).

3-{1-(2,4-dinitrophenyl)-5-[2-(furan-2-yl)ethenyl]-2,3-dihydro -1H-pyrazol-3-yl}prop-2-enehydrazide ⁽⁹⁾ (3)

A mixture of pyrazole (0.01mole) and hydrazine hydrate (0.01mole) in (20ml) ethanol was refluxed for 4hr. the result was filtered and recrystallized from ethanol to yield (3).

N'-[4-(dimethylamino)benzylidene]-3{1,4-(dinitrophenyl)-5-[2-(furan-2-yl)ethenyl]-2,3-dihydro-1H-pyrazol-3-yl}prop-2-enhydrazide⁽¹⁰⁾ (4)

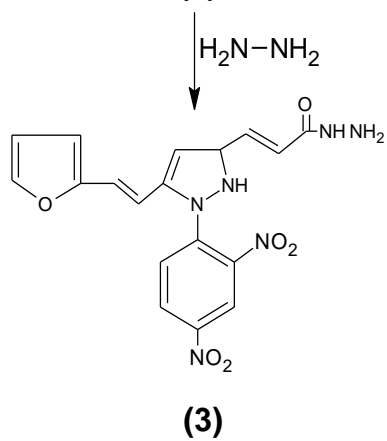
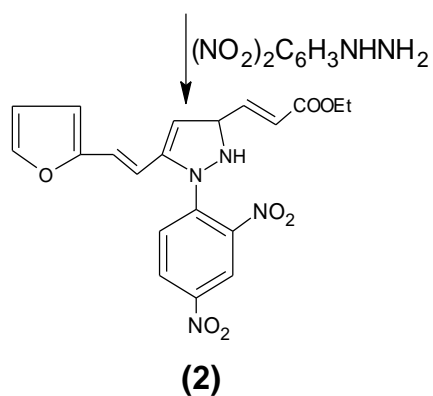
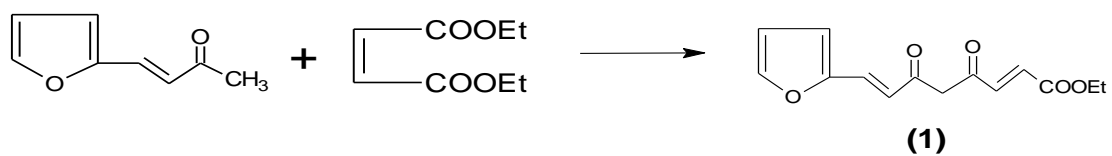
A mixture of an equimolar amount of (3) and benzaldehyde in ethanol (20ml) was refluxed for 2hr. the result was concentrated, cooled and filtered and recrystallized from ethanol to yield (4) in needles.

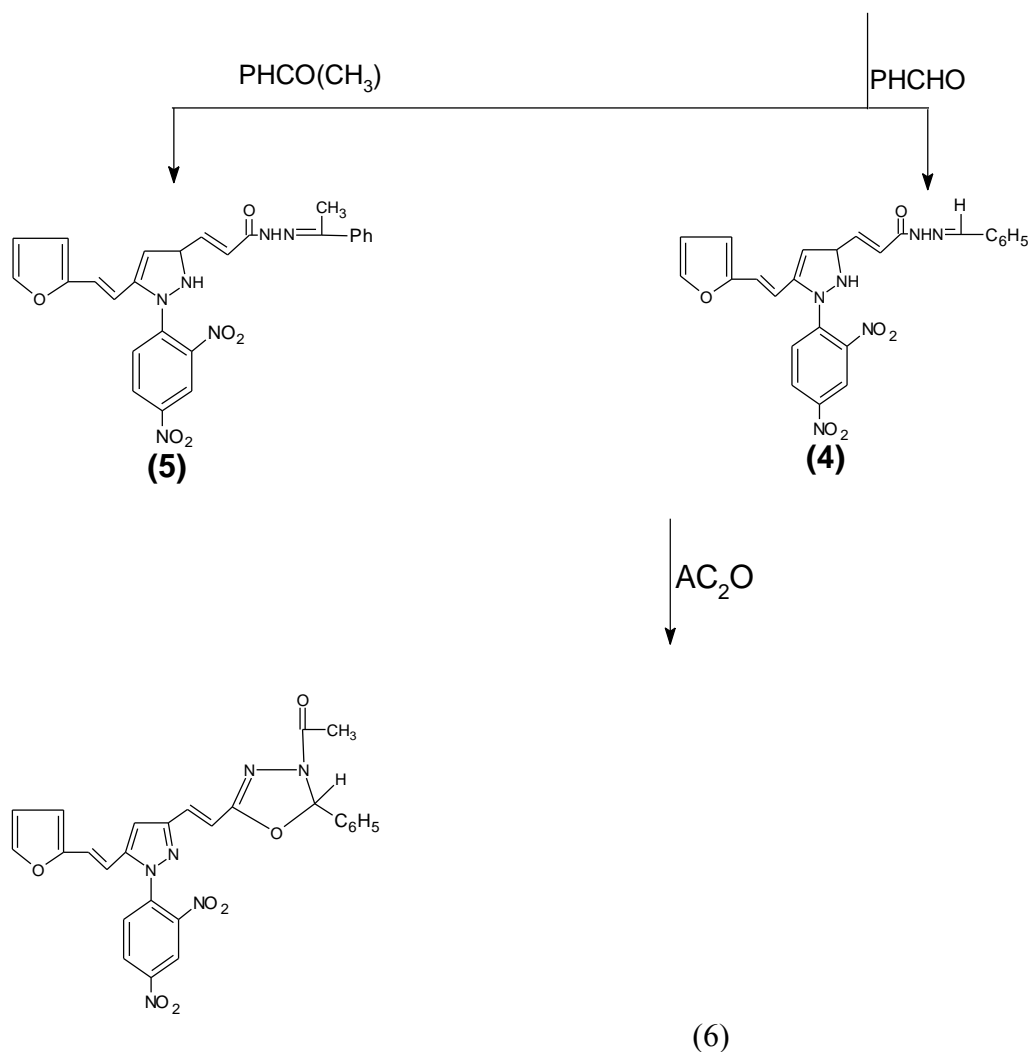
N'-(1-phenylethylidene)-3{1-(2,4-dinitrophenyl)-5-[2-(furan-2-yl)ethenyl]-2,3-dihydro-1H-pyrazole-3-yl}prop-2-enhydrazide⁽¹⁰⁾ (5)

A mixture of an equimolar amount of (3) and acetophenone in ethanol (20ml) was refluxed for 2hr. the result was concentrated, cooled and filtered and recrystallized from ethanol to yield (5) in needles.

5-{2-[5-(2-furan-2-yl)-1-ethenyl]-1-[(2,4-dinitrophenyl)-1H-pyrazole-3-yl]-1-ethenyl}-2-(4-dimethylaminophenyl)-2-hydro-3-acetyl-1,3,4-oxadiazole⁽⁶⁾ (6)

A mixture of the appropriate pyrazole (4) (0.01 mole) and acetic anhydride (5 ml) was refluxed for 3hr. After the reaction of mixture has attained and kept in room temperature and poured into iced cold water. The separated solid was filtered and recrystallized it from ethanol to yield (6).





DISCUSSION :-

The (F.T.I.R) spectrum of starting material (4-(furan-2-yl) but-3-en-2-one)(aliphatic ketone), show absorption band appears at $(1728) \text{ cm}^{-1}$ recourse to $(\text{C}=\text{O})$ bond, and this compound may have enolization epithets, therefore, the broad band can be seen at $(3363-3494) \text{ cm}^{-1}$, due to the hydrogen and oxygen bonding.

Ethyl (8-(furan-2-yl)-4, 6-dioxoocta-2, 7-dienoate (1)

This compound has been diagnosed by using the (F.T.I.R.) spectrum, where absorption band appears at $(1720) \text{ cm}^{-1}$ recourse to $(\text{C}=\text{O})$ bond for ester, and absorption band appears at $(1640) \text{ cm}^{-1}$ recourse to diketone structure $(\text{CO}-\text{CH}_2-\text{CO})$, this structure have enolization epithets, therefore, the broad band can be seen at $(3380-3440) \text{ cm}^{-1}$ recourse to transformation of the above structure to enol structure $(\text{CO}-\text{CH}=\text{COH})^{(11)}$. Also absorption band appears at $(1340) \text{ cm}^{-1}$ recourse to $(\text{C}-\text{O})$ bond for α, β -unsaturated ester and also for $(\text{C}-\text{O}-\text{C})$ bond. The physical properties of

[Ethyl Octanoate (1)] in table (1) and the table (2) shows the other important bands for (F.T.I.R) spectrum.

The (U.V.) spectrum of ester (1) show maxima absorption at (316) nm, recourses to interfere between ($n-\pi^*$) and ($\pi-\pi^*$) transfers due to the succession between (C=O) and (C=C) bonds, for dienone structure in the ester compound.

Ethyl-3-{ 1-(2, 4-dinitrophenyl)-5-[2-(furan-2-yl) ethen- yl] -2, 3-dihydro-1*H*-pyrazol-3-yl} prop-2-enoate (2)

The (F.T.I.R) for this compound, shows absorption band appears at (1708) cm^{-1} recourses to (C=O) bond, and binary absorption band appears at (3321-3363) cm^{-1} recourses to (N-H) bond in pyrazole circle, also absorption band appears at (1334) cm^{-1} recourses to aromatic (NO_2) group, and absorption band at (1215) cm^{-1} recourses to (C-N) bond in pyrazole circle as well at (972) cm^{-1} to (C-N) bond for substitution (NO_2) on benzene circle. The physical properties in table (1), table (2) show the other important bands for (F.T.I.R) spectrum.

3-{ 1-(2,4-dinitrophenyl)-5-[2-(furan-2-yl)ethenyl]-2,3-dihydro -1*H*-pyrazol-3-yl}prop-2-enediazide (3)

The chart of (F.T.I.R) spectrum, for this compound, shows new broad absorption band appearance at (3420-3440) cm^{-1} recourses to ($-\text{NH}_2$) group and still binary absorption band at (3320-3360) cm^{-1} which recourses to ($-\text{NH}$) group, also still absorption band for (NO_2) group at (1350) cm^{-1} , while (C=O) bond appeared at (1650) cm^{-1} this band less than (C=O) bond band of aldehydes and ketones due to adhesion it with nitrogen atom which causes shift in vibration to the less than (1720 cm^{-1}) it name amide bond. The physical properties in table (1), table (2) show the other important bands for (F.T.I.R) spectrum.

The (U.V) spectrum of the above compound, shows maxima absorption at (318) nm, recourses to ($\pi-\pi^*$) transfers, and maxima absorption at (379) nm, recourses to ($n-\pi^*$) transfers this absorption shifted towards the longer wavelength from compound (1) due to the succession between (C=O) and ($-\text{NH}$) bonds.

N'-[4-(dimethylamino)benzylidene]-3{ 1,4-(dinitrophenyl)-5-[2-(furan-2-yl)ethenyl]-2,3-dihydro-1*H*-pyrazol-3yl}prop-2-enhydrazide (4)

We note that the vibration of (NH_2) group is weak in this compound due to formation Schiff base, and the binary absorption band was still at (3274-3321) cm^{-1} which recourses to ($-\text{NH}$) group, also still vibration of (C=O) bond at (1625) cm^{-1} , and absorption band appearance at (1596) cm^{-1} recourses to azomethen group (C=N). The physical properties in table (1), table (2) show the other important bands for (F.T.I.R) spectrum.

The (U.V) spectrum, show maxima absorption at (293) nm, recourses to ($\pi-\pi^*$) transfers, and maxima absorption at (374) nm, recourses to ($n-\pi^*$) transfers.

N'-(1-phenylethylidene)-3{ 1-(2,4- dinitrophenyl)-5-[2-(furan-2-yl)eyhenyl]-2,3-dihydro-1*H*pyrazole-3yl}prop-2-enhydrazide (5)

We note that the vibration of (NH₂) group is weak too in this compound due to formation Schiff base, and the binary absorption band stay at (3300-3380) cm⁻¹ which recourses to (-NH) group, also still vibration of (C=O) bond at (1625)cm⁻¹. The physical properties in table (1), table (2) show the other important bands for (F.T.I.R) spectrum.

The (U.V) spectrum, shows maxima absorption at (293) nm recourses to (π - π^*) transfers, and maxima absorption at (396) nm recourses to (n- π^*) transfers.

1-(2,4-dinitrophenyl)-3-(2-phenyl-2-hydro-3-acetyl-1,3,4-oxa diazol-5-yl)-5-[2-(2'-furyl)ethen-1-yl] Pyrazole (6)

The chart of (F.T.I.R) spectrum, for this compound, shows also the binary absorption band stay at (3320-3360cm⁻¹) which recourses to secondary(N-H)bond and absorption band appearance at(1640cm⁻¹) recourses to (C=O) bond due to it amide bond, this band less than (C=O) bond band of aldehydes and ketones due to adhesion it with nitrogen atom which causes shift in vibration to the less than (1720cm⁻¹),due to the resonance between them, and absorption band appearance (1480-1510) cm⁻¹ recourses to (C=N) bond. The physical properties in table (1), table (2) show the other important bands for (F.T.I.R) spectrum.

The (U.V) spectrum, shows maxima absorption at (293) nm, recourses to (π - π^*) transfers, and maxima absorption at (396) nm, recourses to (n- π^*) transfers.

Table (1) physical properties of compounds

Compound	Molecular formula	Solvent	Yield %	R _f %	m.p.C°	Color
α,β -unsaturated aliphatic ketone	C ₈ H ₈ O ₂	Ethanol	71	0.84	35-36	Light yellow
1	C ₁₄ H ₁₄ O ₅	Ethanol	67	0.687	115-116	Dark yellow
2	C ₂₀ H ₁₈ N ₄ O ₇	Ethanol	84	0.743	142-143	Pink
3	C ₁₈ H ₁₆ N ₆ O ₆	Ethanol	82	0.881	187-188	Dark gray
4	C ₂₇ H ₂₅ N ₇ O ₆	Ethanol	92	0.853	136 dec.	Light brown
5	C ₂₆ H ₂₂ N ₆ O ₆	Ethanol	93	0.778	157 dec.	Dark brown
6	C ₂₉ H ₂₅ N ₇ O ₇	Ethanol	69	0.796	166-167	Brown

able (2) (F.T.I.R) spectra of compounds

Comp.	C-H aromat cm ⁻¹	C-H aliphatic cm ⁻¹	C=C aromatic cm ⁻¹	C=N cm ⁻¹	Other
α,β -unsaturated aliphaticketone	3010	2940	1620	—	(C-O-C) 1361cm ⁻¹
1	3120	2940	1625	—	(C-O-C) and (COOCH ₃) 1340cm ⁻¹
2	3100	2910	1616	—	(C-N) 1215-1307cm ⁻¹ (NO ₂) 1334cm-1
3	3110	—	1620	—	(C-N) 1210-1315cm ⁻¹ (NO ₂) 1350cm ⁻¹
4	3109	2920	1596	1512	(NO ₂) 1330 cm ⁻¹ (C-N) 1303 cm ⁻¹
5	3120	2920	1596	1508	(NO ₂) 1330 cm ⁻¹ (C_N) 1303 cm ⁻¹
6	3110	3080	1620-1590	1510	(NO ₂) 1330 cm ⁻¹ (C-N) 1255 cm ⁻¹

Fig. (1) (F.T.I.R) spectrum of starting materia
(α,β -unsaturated alepatic ketones)

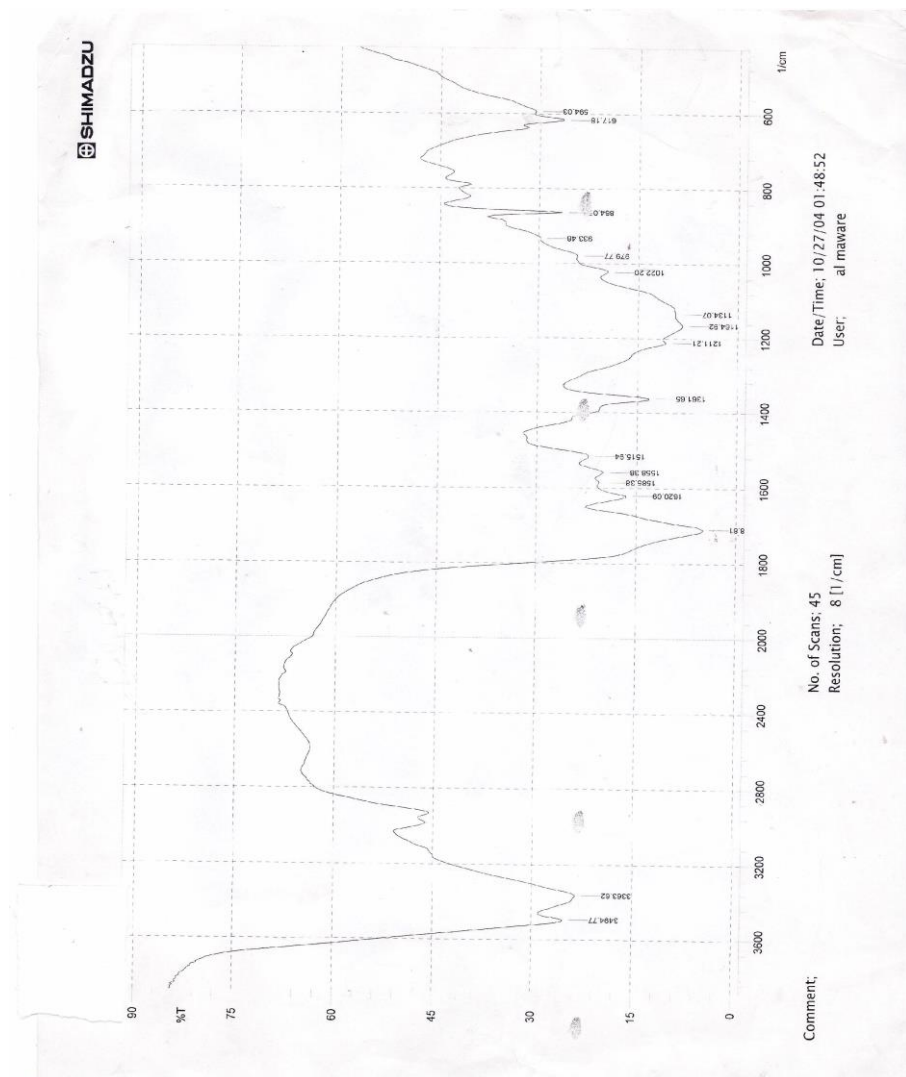


Fig. (2) (F.T.I.R) spectrum of compound (1)

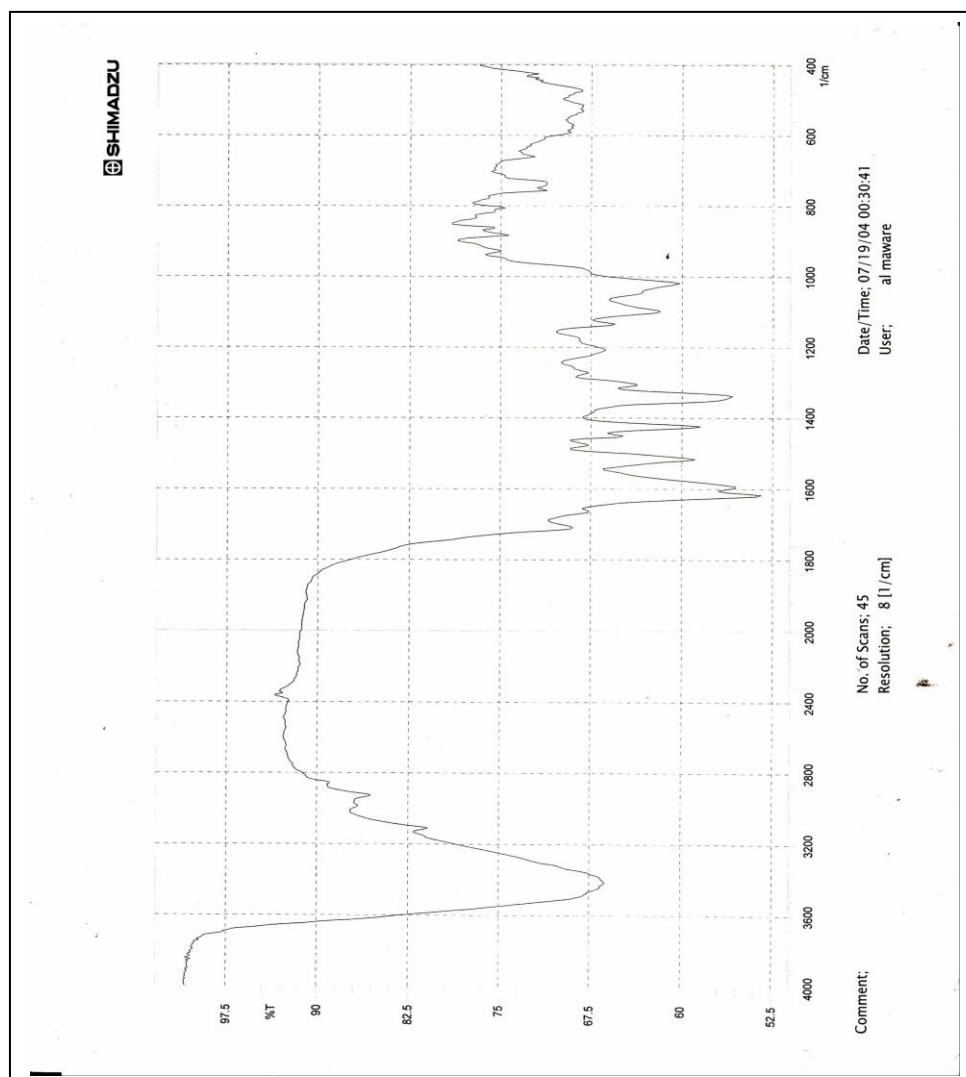


Fig. (3) and (U.V) spectrum of compound (1)

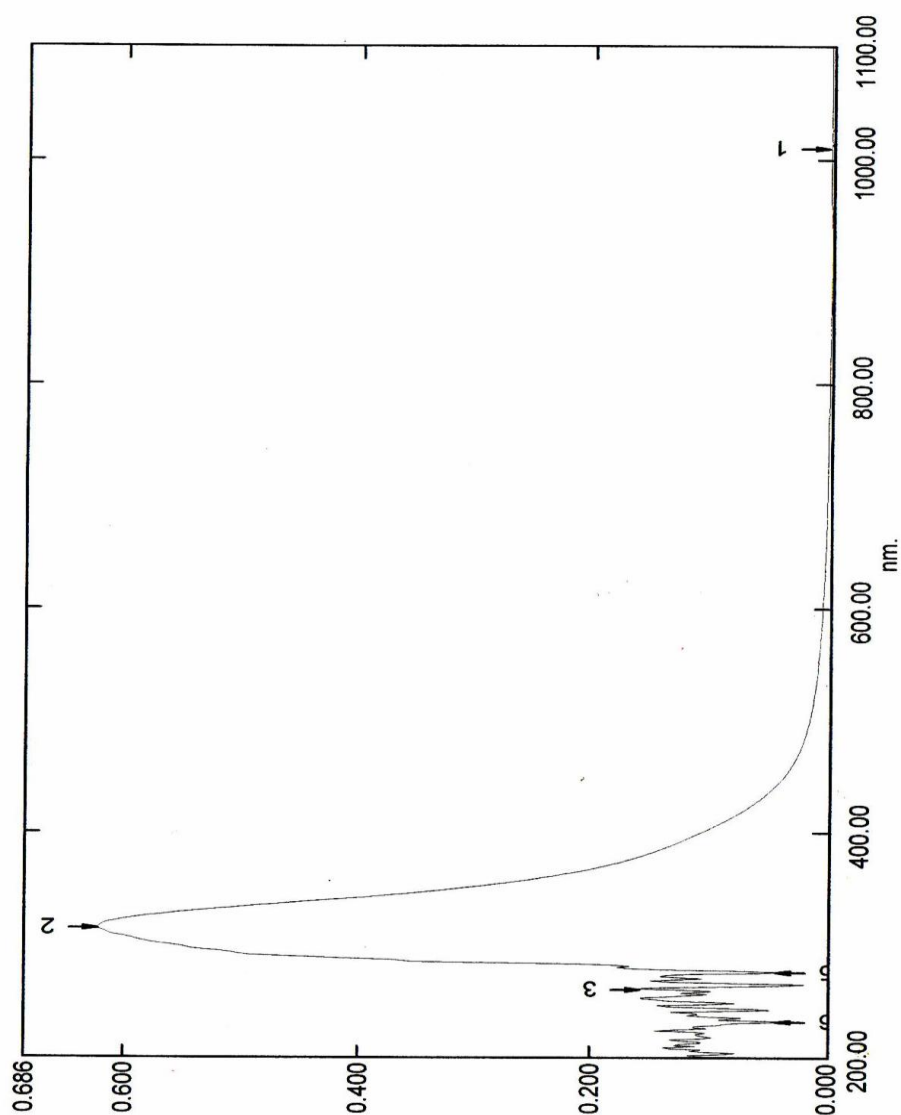


Fig.(4) (F.T.I.R) spectrum of compound (2)

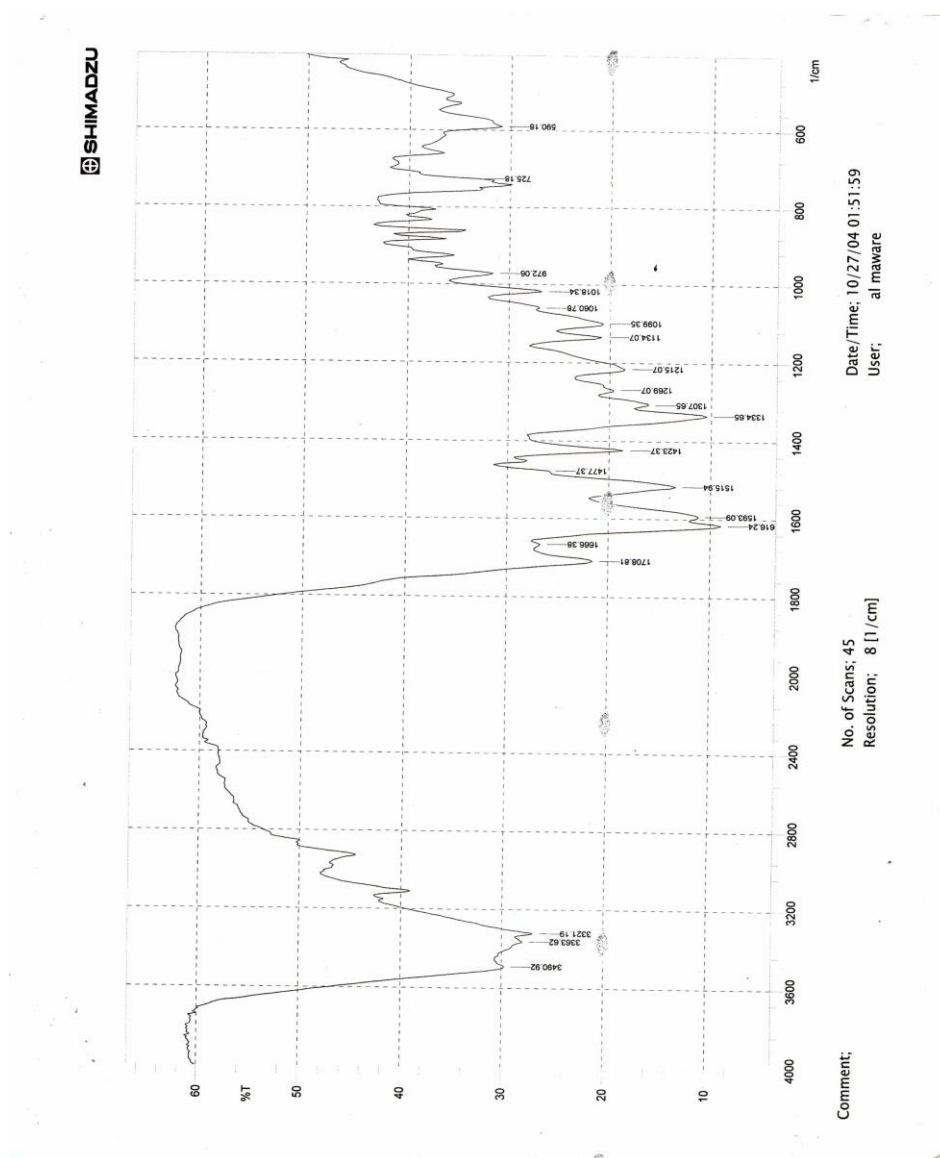


Fig.(5) (U.V) spectrum of compound (2)

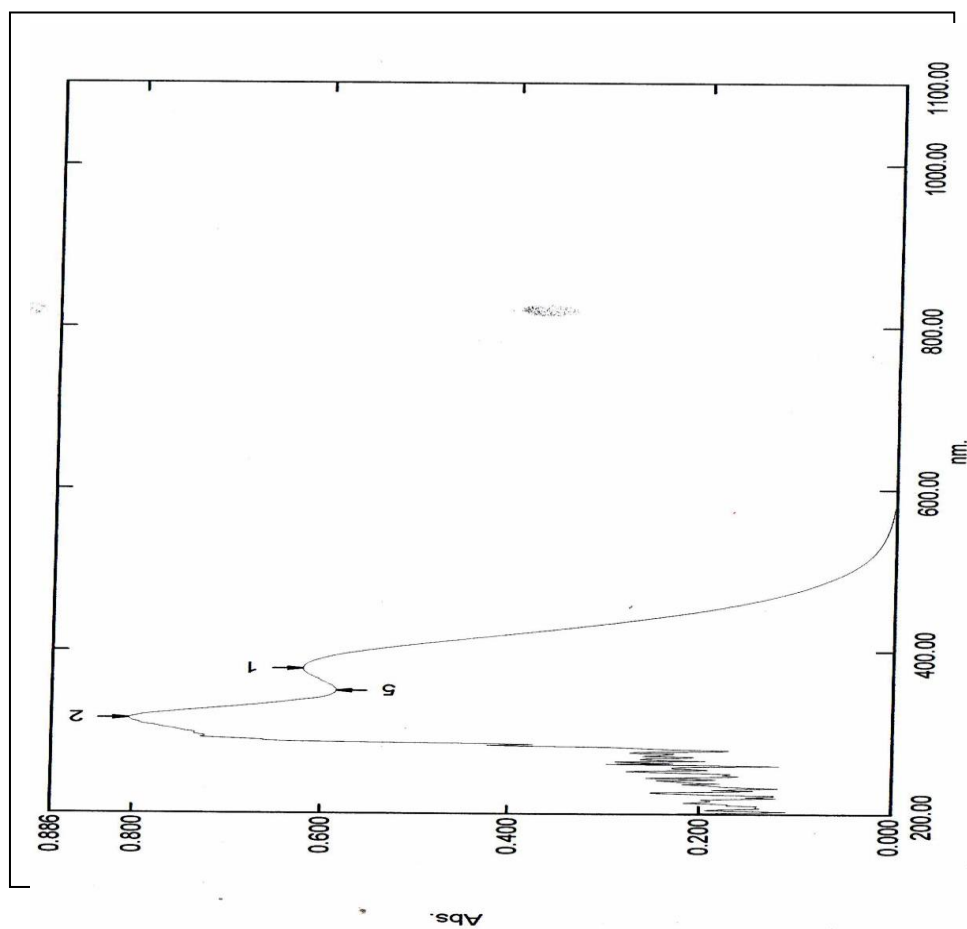


Fig.(6) (F.T.I.R) spectrum of compound(3)

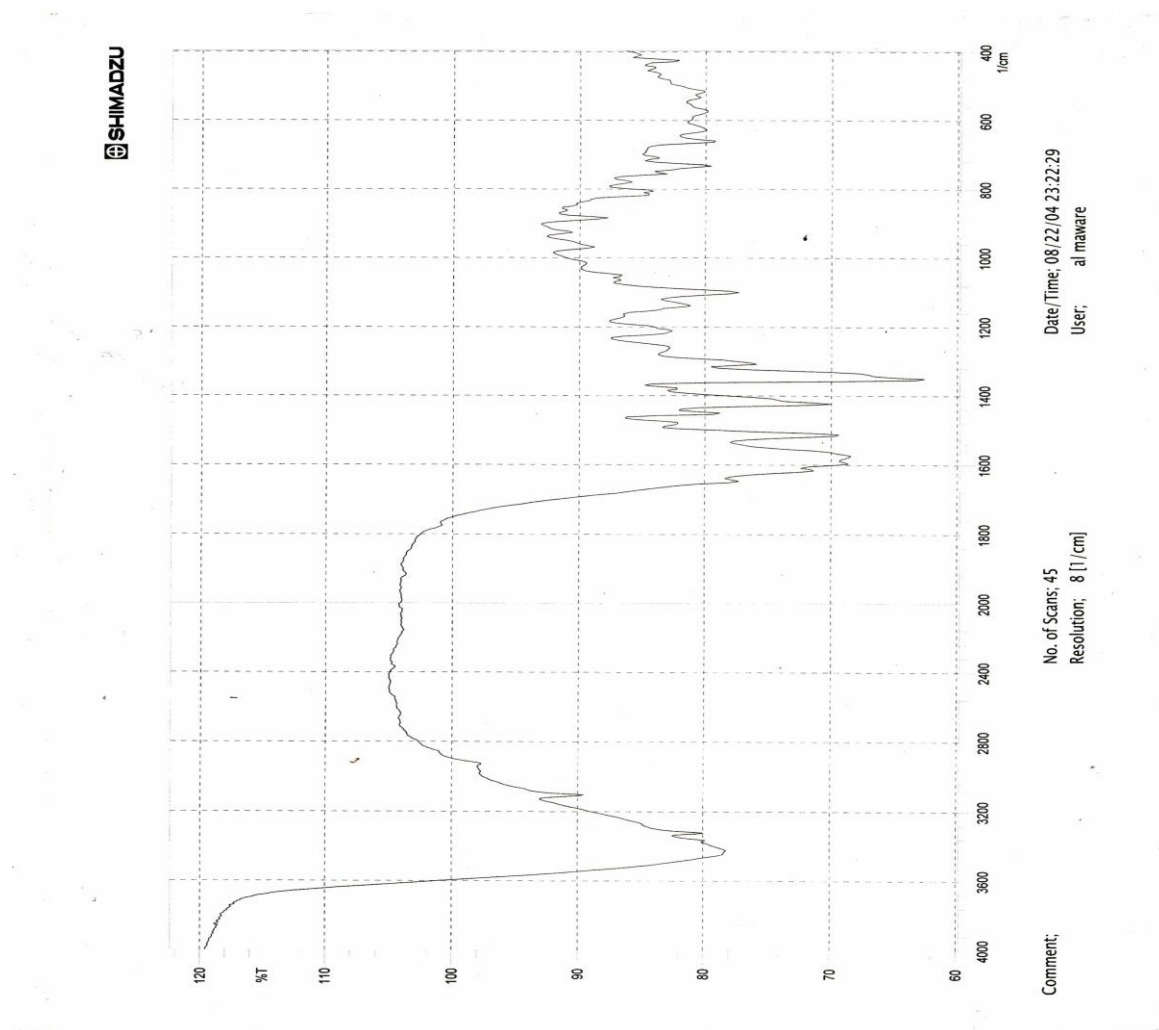


Fig.(7) (U.V) spectrum of compound (3)

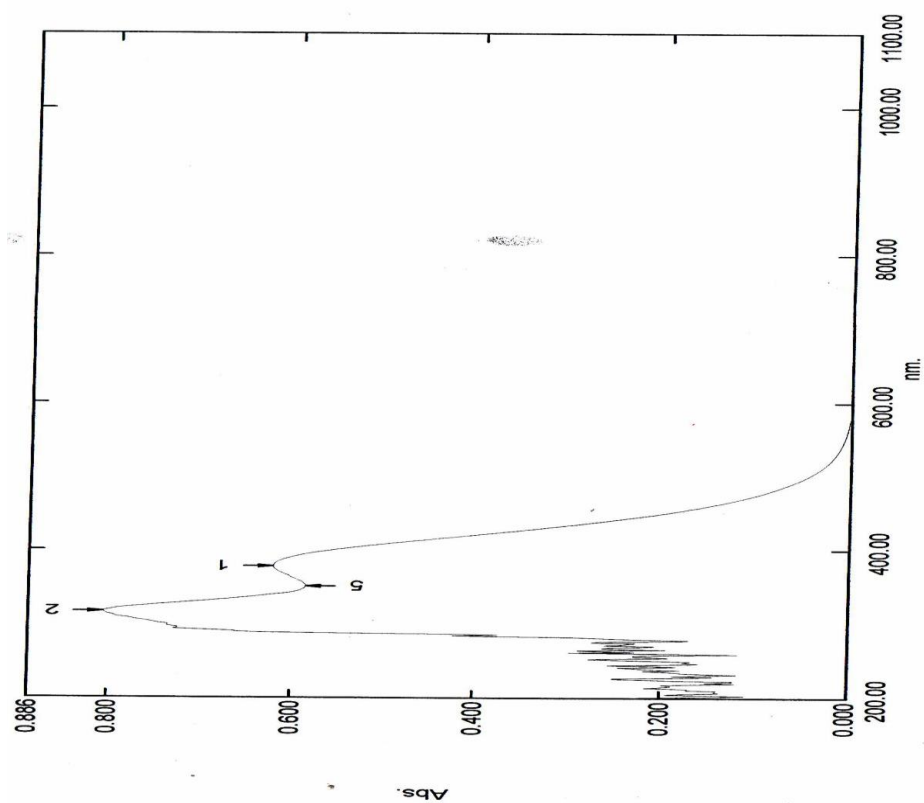


Fig.(8) (F.T.I.R) spectrum of compound (4)

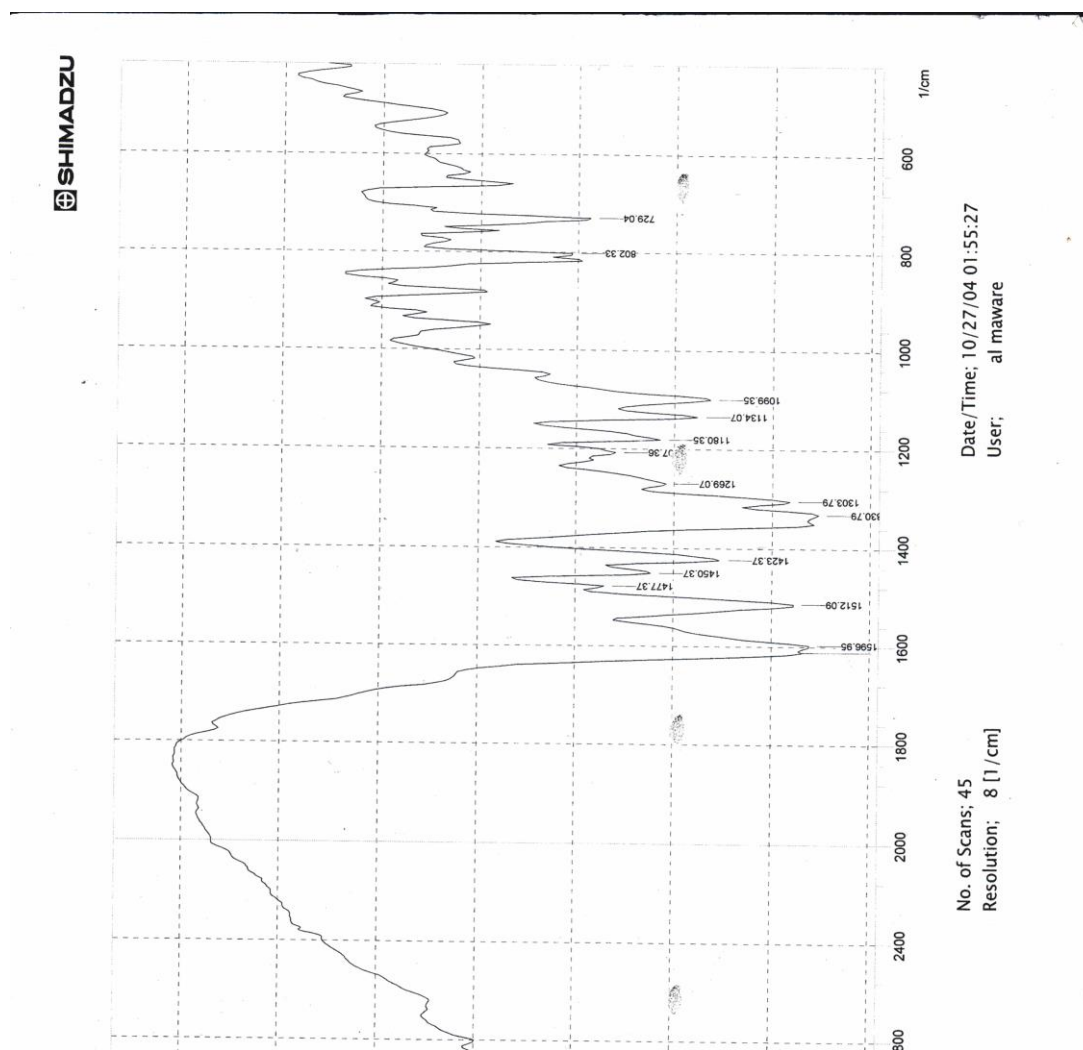


Fig.(9) (U.V) spectrum of compound (4)

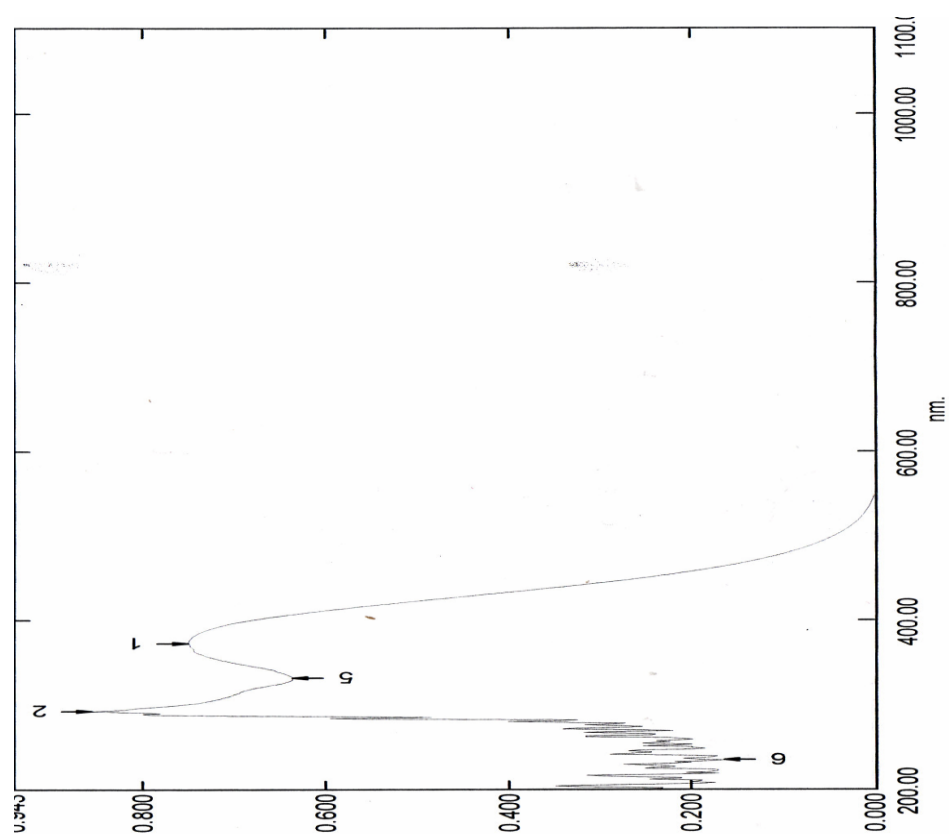


Fig.(10) (F.T.I.R) spectrum of compound (5)

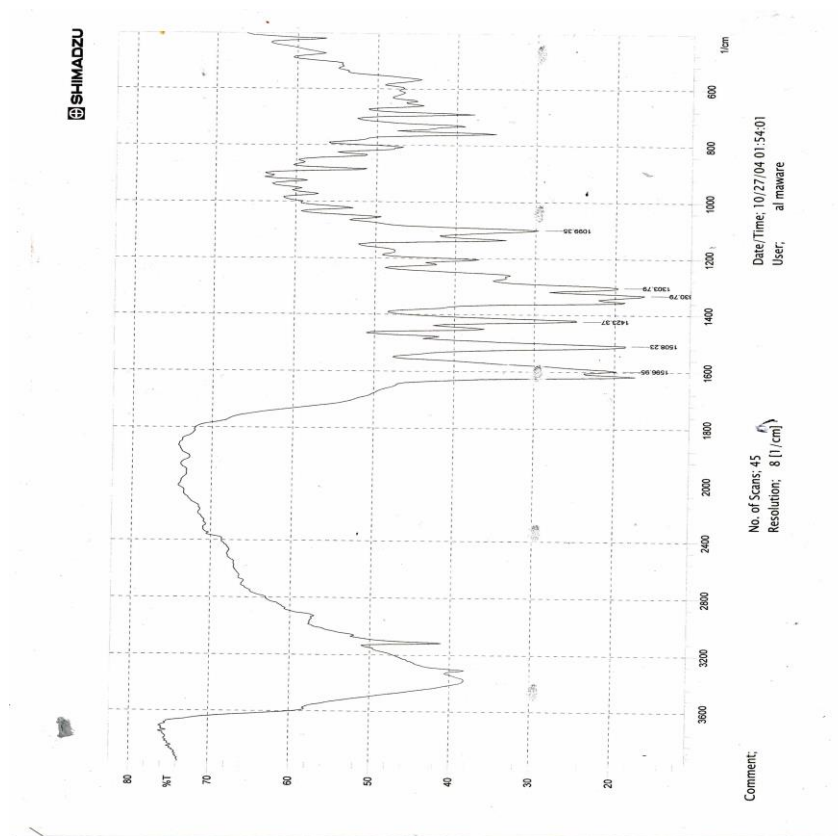


Fig.(11) (U.V) spectrum of compound (5)

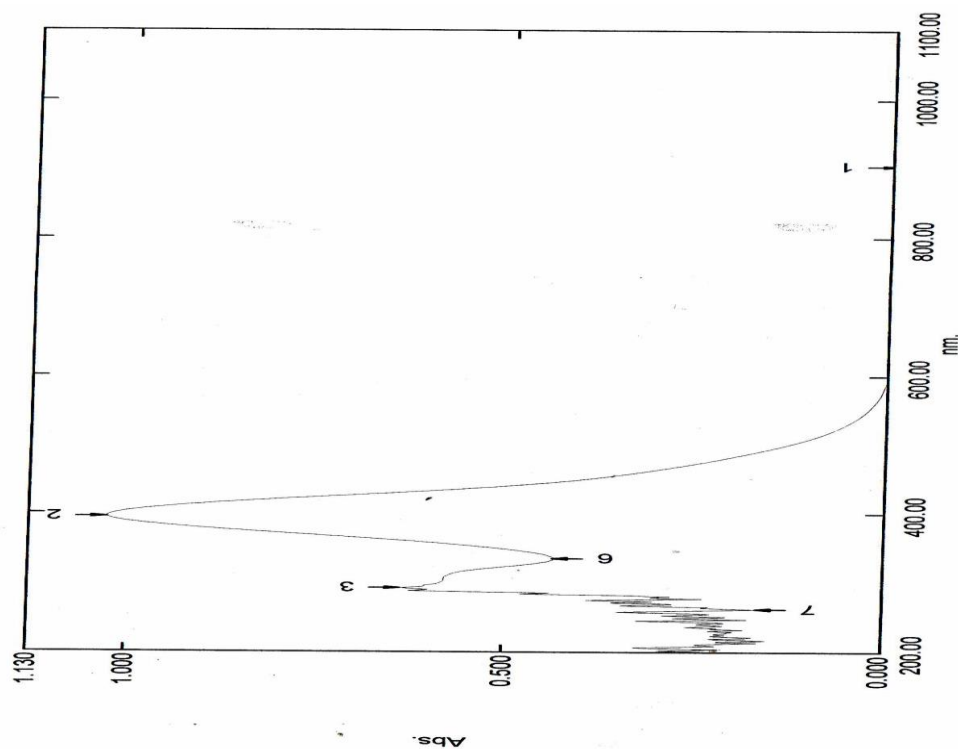


Fig.(12) (F.T.I.R) spectrum of compound(6)

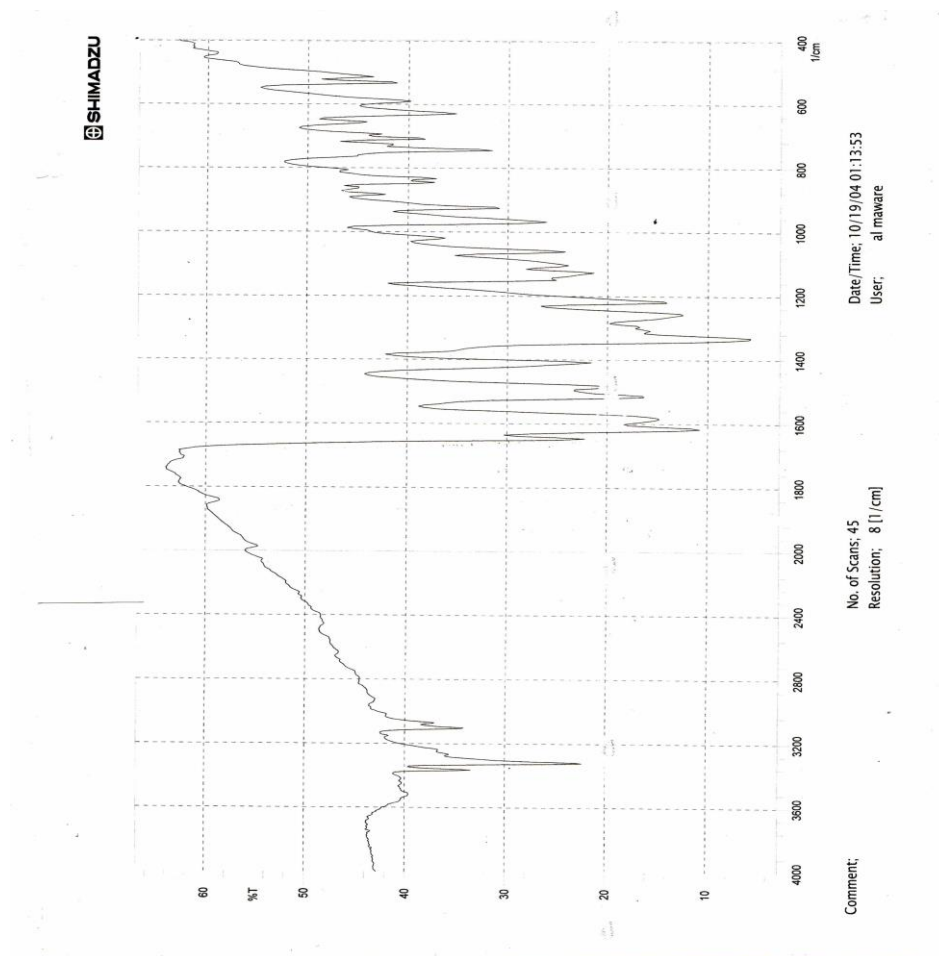
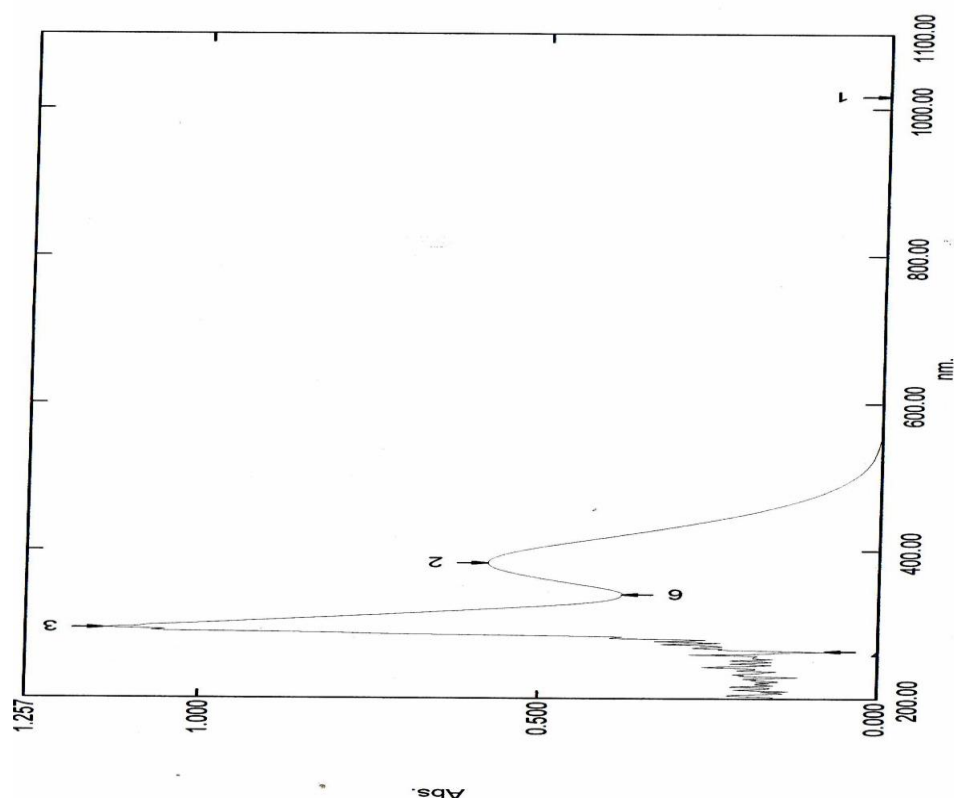


Fig.(13) (U.V) spectrum of compound (6)



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تحضير وتشخيص بعض مشتقات الكيتونات غير المشبعة في الموقع α و β

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قسم الكيمياء/كلية التربية/جامعة القادسية/العراق 2009

الخلاصة:

المركب الأساس 4-(فيوران-2-يل)-3-بيوتين-2-اون (كيتون ألفاتي) حُضر بمعاملة الفورفورالديهيد مع الأسيتون، والذي تفاعل مع المركب ثنائي اثيل مالات ليعطي المركب ثنائي كيتو استر (1)، ثم حُول المركب (1) إلى مشتق البايرازول (2) بمفاعله مع المركب (2،4-ثنائي نايتروفنيل هيدرازين). مشتق البايرازول (2) تفاعل مع الهيدرازين المائي ليعطي حامض الهيدرازيد (3)، ثم تفاعل الحامض مع الالديهيدات (بنزالديهيد) لينتج قاعدة شيف (4) ومع الكيتونات (اسيتوفينون) لينتج قاعدة شيف (5). قاعدة شيف (4) حُولت إلى حلقة الاوكسادايازول (6) بمفاعله مع انهيدريد ألكليك.