



KNOEVENAGEL CONDENSATION OF 5-SUBSTITUTED FURAN-2-CARBOXALDEHYDE WITH INDAN-1,3-DIONE

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Abstract

A series of new heterocyclic compounds of 2-(5-substituted -Furfurylidene)-Indane-1,3-dione, were prepared and identified by their melting points, Infrared, Ultraviolet, and Nuclear magnetic resonance spectra.

Key words: Knoevenagel condensation, Furfurylidene, Indan-1,3-dione

تكايف نوفيناجيل لمشتقات ٥-فيوران-٢-كاربوكسالدهيد مع مركب الاندان-١,٣-دايون

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قسم الكيمياء، كلية العلوم، جامعة دمشق

الخلاصة

تم تحضير سلسلة جديدة من المركبات الحلقية غير المتجانسة من ٢-(٥-معيوض فورفورلدين)-انندان-١,٣-دايون بواسطة تكايف مشتقات الفورفورال مع مركب الاندان ١,٣-دايون تم تشخيص المركبات المحضرة بواسطة تعيين درجات انصهارها وقياسات الاطيف تحت الحمراء وفوق البنفسجية، وطيف الرنين النووي المغناطيسي

الكلمات المفتاحية: تكايف نوفيناجيل بفورفورال بفورفورلدين. انندان-١,٣-دايون

Introduction:

One of the most important objects of Knoevenagel condensation from a synthetic perspective is that they offer a route to the formation of C=C bond, by which the arylidene compounds are obtained from carbonyl compounds and active methylene compounds [1-3], in the presence of basic catalyst or Lewis acid catalyst, such as piperidine, diethylamine, or corresponding ammonium salt. [4-8]. In recent years there has been a growing interest in Knoevenagel condensation products because many of them have significant biological activity [9-13], this reaction has been widely used in organic synthesis to prepare coumarins and its derivatives, which are important intermediates in the preparation of cosmetics, perfumes, and pharmaceuticals [14,15]. Furfural and its 5-substituted derivatives were chosen as being synthetically versatile

molecules with a reactive carbonyl group, they have considerable significance for their biological activities [16-19] and for their reactivity toward nucleophiles which allows the synthesis of a wide variety of heterocyclic such as nifuroxazide (NF) (condensation of 5-nitro furfural with p-hydroxybenzhydrazide) [20], which is used for the treatment of acute bacterial diarrhea [21]. In addition to that, β -dicarbonyl compounds have been studied intensively owing to their synthetic and biological significance and as well known indan-1,3-dione derivatives are important as anti-coagulant drugs or rodenticides in hepate. [22] In addition to anticoagulant effect and rodenticidal activity. These compounds have shown parasiticidal effects, [23] analgesic, herbicidal [24]. This work involves preparation and identification of some new substituted

Furfurylidine indan-1,3-dione a heterocyclic derivatives of Furfural .

Experimental

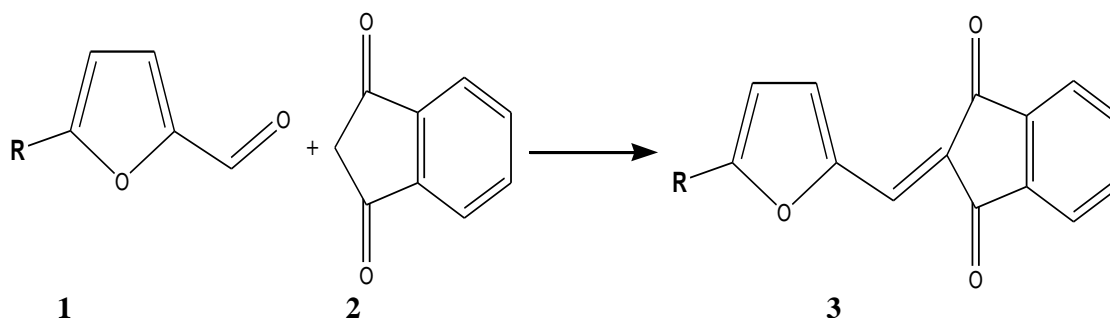
Prepared compounds were characterized by UV, ¹H-NMR and IR spectra Table a(1-3). The melting points were determined on a Kofler Block apparatus and are uncorrected. Infrared spectra were recorded in 400 - 4000 cm⁻¹ region by a Specord FT-IR Jusco 300 spectrometer using KBr disk. ¹H-NMR Spectra were measured on ambient Broker DT-400 MHz spectrometer in deuterated CDCl₃, and UV-visible were determined with Shimadzu 190 A spectrometer (College of Science –Damascus University). All fine chemicals and reagents were purchased from Aldrich chemical Co. U.S.A. Furfural were pre-distilled and dried appropriately prior to use

Synthesis of 3a-3d

A mixture of 5-substituted-furfural 1a-1d (5 mmol), Indan-1,3-dione (2) (5 mmol) in ethanol (10 cm³) and (10 cm³), was stirred with simple heating until the solid was dissolved then stirred at room temperature for the time given in Table(1). The solid precipitate was filtered. The products were recrystallized from ethanol or acetic acid.

Results and Discussion

A four 2-(5-substituted furfurylidene) Indane-1,3-diones (3a-3d) were obtained by condensations of some 5-substituted Furfural (1a-1d) with Indane-1,3-diones (2) in ethanol, at room temp. The yield of prepared compounds were ranged between (46-72%). Table(1) show some properties of these compounds



Where R= a: H , b: C₂H₅ , c: I , d :NO₂

¹H-NMR spectra of these compounds [Figs 1-4], indicate a disappearance proton signals at δ (4.10) ppm for the (methylene and aldehyde groups) of compounds (1 and 2), and appearance of a proton signal of olefine α -proton (H α) [structure 4] at (7.7-7.8) ppm for all prepared compounds. Also ¹H-NMR spectral analysis shows proton signals of aromatic and furan rings at δ (6.4-8.6) ppm as in (Table 2). All condensation products are stable solid compounds, rather insoluble in common solvents, with high melting points. The resonance signals and their multiplicity confirmed the proposed structures. The infrared spectra of the prepared compounds (3a-3d) showed strong absorption bands of the C=C and

C=O stretching vibrations in two very well distinguished regions (1610 – 1680) cm⁻¹ and (1690-1758) cm⁻¹ (Table 3). The absorption bands in the lower region of the spectra (1400-1600) cm⁻¹ belong to the ν (C=C) of the furan and aromatic-rings. The compound 3d showed the ν (C=C) band at a lower frequency (1627) cm⁻¹, due to the presence of withdrawing nitro group and its conjugation effect with furan ring [25]. (Table 1). UV spectra showed red-shift phenomena for all prepared compounds attributed to the conjugated of furan ring with C=C bond formed, table(1). Where λ_{max} for furfural is (329nm) while λ_{max} for indan is (358nm).

Table 1: Characterization of the prepared compounds

Comp.	R	NO.of gm. used	Formula <i>M.wt</i>	m.p. °C	Colore	Yield %	Tr(Stirr.) (hr)	$\lambda_{max,n.m}$ <i>F.u.r,indan</i>
3a	H	0.48	C ₁₄ H ₈ O ₃ 224.21	203-205	yellow	50	2.5	366,390
3b	C ₂ H ₅	0.62	C ₁₆ H ₁₂ O ₃ 252.26	105-107	yellow	46	5	395,398
3c	I	0.89	C ₁₄ H ₇ IO ₃ 350.11	195-197	Dark yellow	68	3	396,405
3d	NO ₂	0.7	C ₁₄ H ₇ NO ₅ 269.21	189-191	Pale orange	72	0.75	372,385

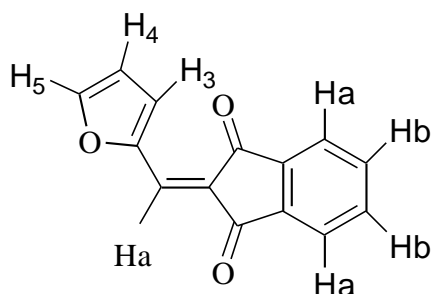


Table 2: ¹H NMR spectral data of prepared compounds, in CDCl₃

COMP.	¹ H NMR spectrum ppm
3a	δ : 7.78 (s, 1H, Ha); 7.78, 7.79-7.82, 8.61 (7H, 4H-ArH, 3H-furan ring).
3b	δ : 1.35 (t, 3H-C ₂ H ₅); 2.83 (q, 2H, -C ₂ H ₅); 7.73 (s, 1H, Ha); 6.43, 7.77-7.78, 7.97-7.98, 8.6 (6H, 4H-arom. and 2H-furanes) 8.59
3c	δ : 7.72 (s, 1H, Ha); 6.92, 7.79-7.82, 7.97-8.00, 8.46 (6H, 4H-arom. and 2H furanes).
3d	δ : 7.72 (s, 1H, c=cHa); 7.50, 7.88-7.91, 8.05-8.08, 8.62 (6, 4H-arom. and 2H-furanes).

Table 3: IR spectral data of synthesized compounds 3a-3d.

Comp.	ν C=O	ν C=C furan, Ar	ν C=C	others
3a	1745, 1695	1412, 1570	1680	
3b	1758, 1700	1413-1562, 1590	1653	CH aliphatic, 2932
3c	1720, 1690	1425, 1540, 1580	1610	
3d	1730, 1690	1400, 1470, 1590	1627	NO ₂ ; 1348, 1517, [26].

Sample 6_06-12-2010

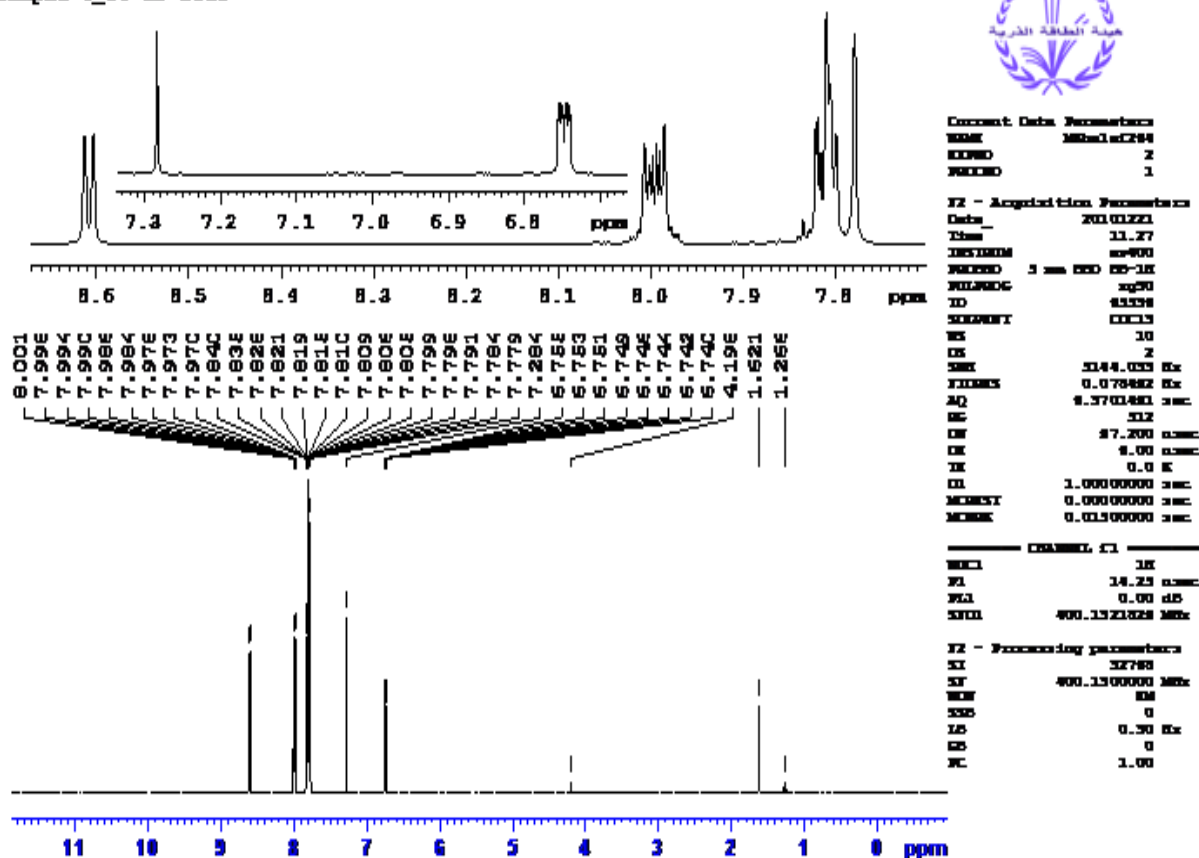


Figure 1: ¹H NMR spectrum of comp.3a

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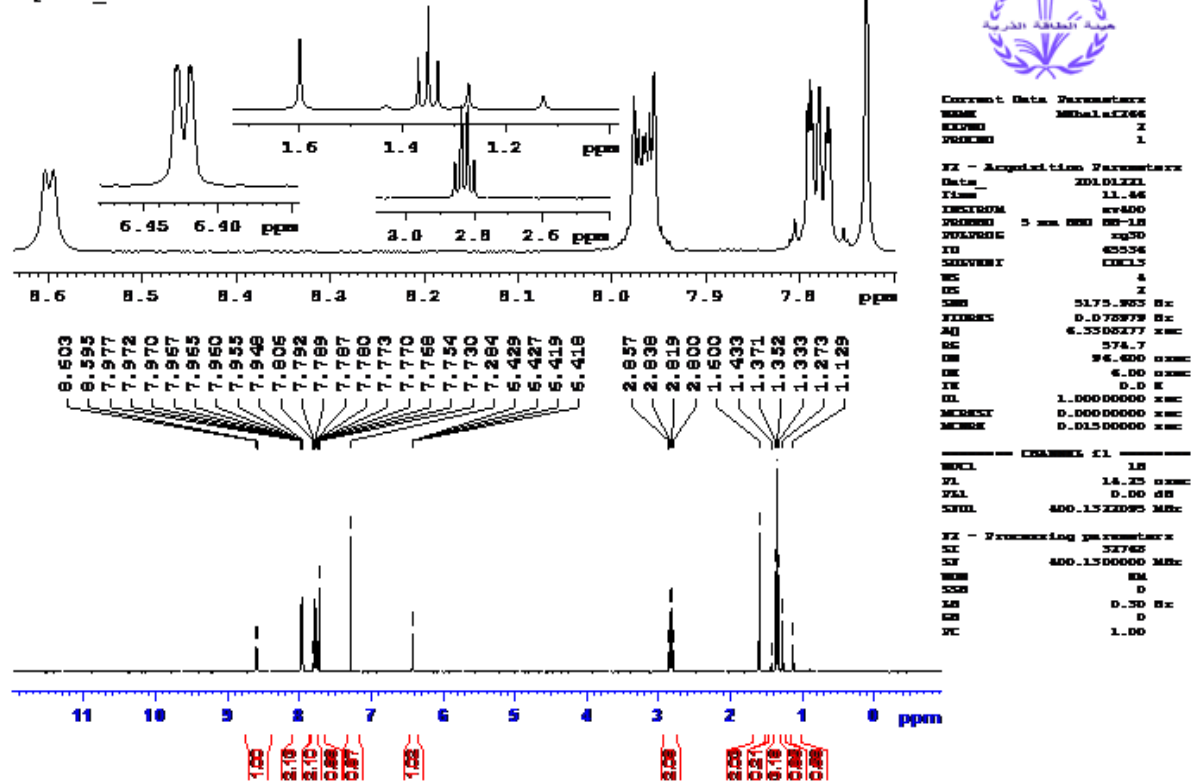


figure 2: ¹H NMR spectrum of comp.3b

Sample 9_06-12-2010

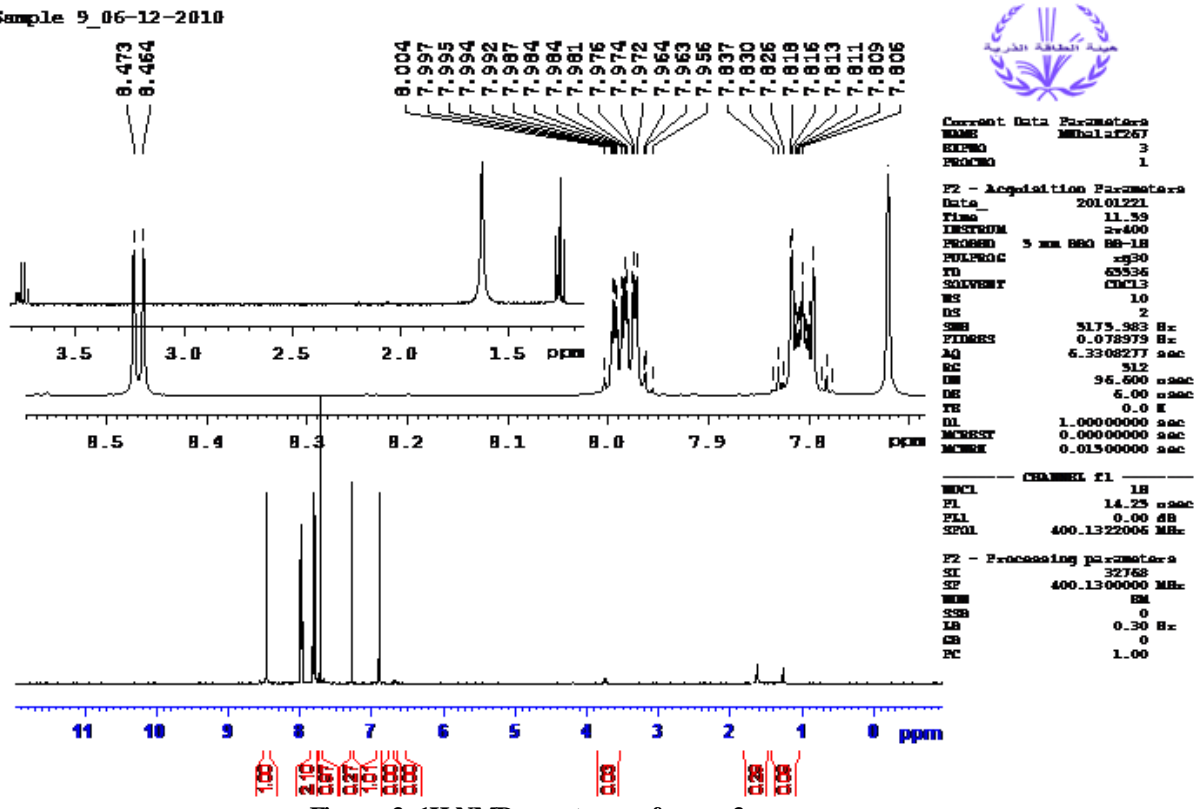


Figure 3: ¹H NMR spectrum of comp.3c

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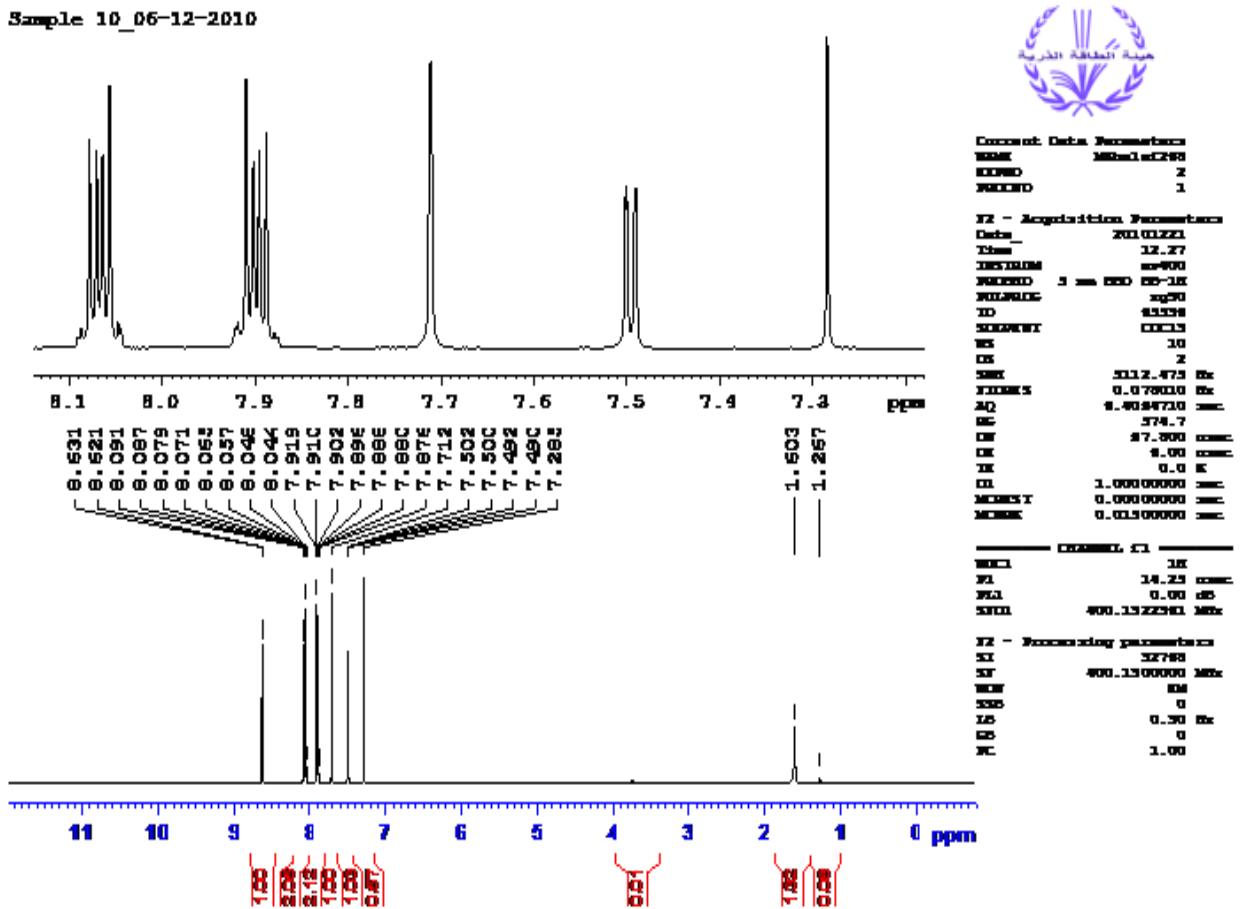


Figure 4: ¹H NMR spectrum of comp.3d56554er

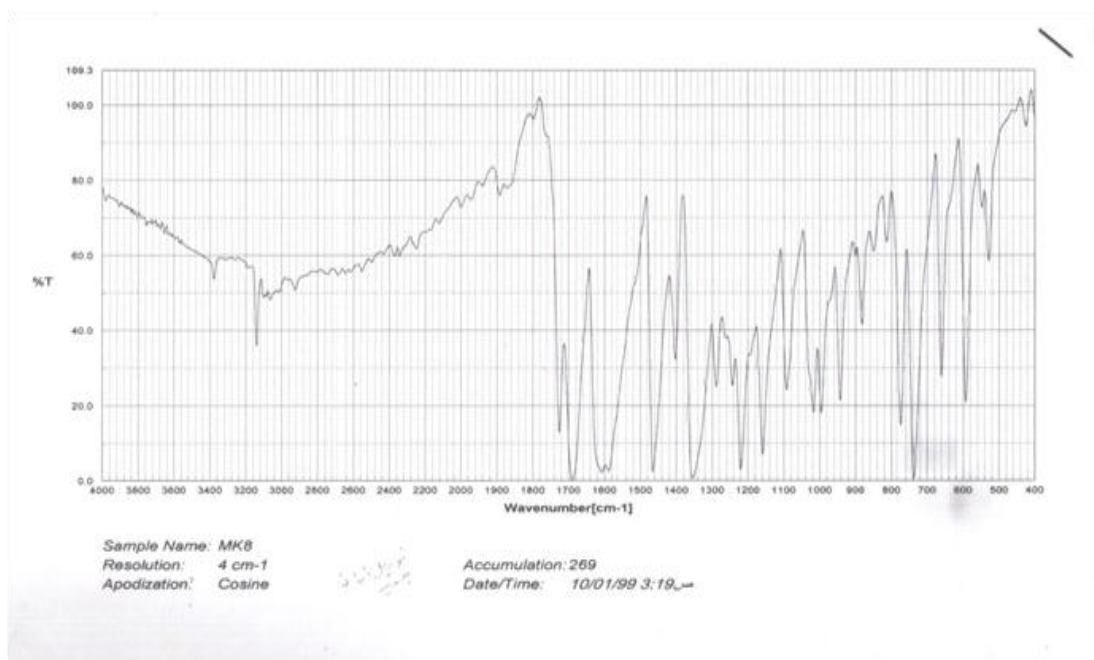


Figure 5: IR spectrum of comp.3a

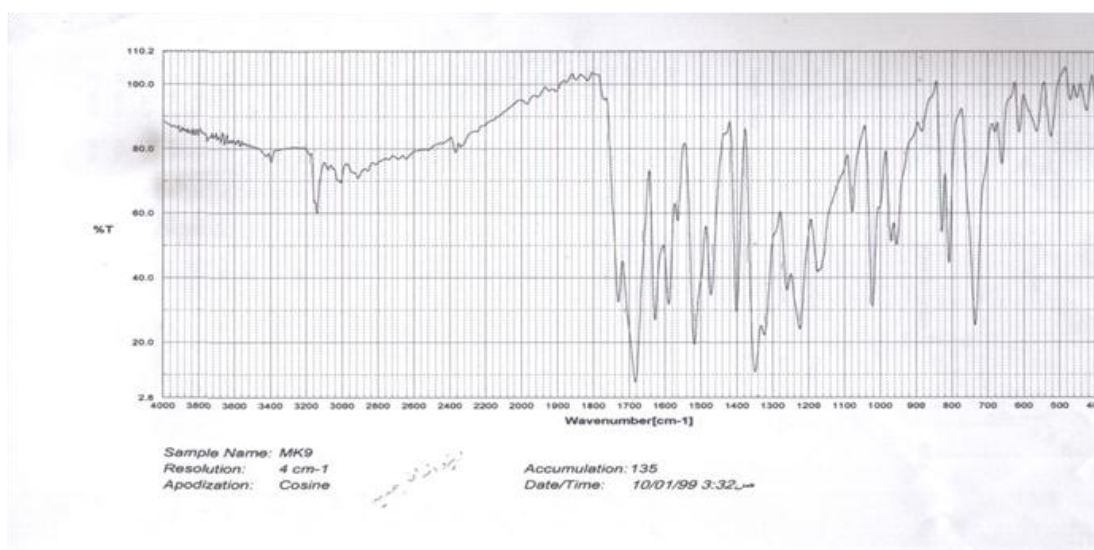


Figure 6: IR spectrum of comp.3d

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