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PREPARATION AND DIAGNOSIS OF NEW AZO - BARBITURATE DYES

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Abstract: -

The research includes the preparation of new azo-barbiturate dyes derived from shiff bases prepared by reaction Barbituric acid & phenlenediamine and repellency bases by means of double-reaction of repellant bases with different phenolic compounds. These compounds were diagnosed using infrared techniques, ultraviolet-visible radiation, NMR proton and thin layer chromatography. All barbiturate dyes had absorption between (273 –310) nm and showed hypsochromic shift from the corresponding azo dyes. The crystal structures of barbiturate dyes indicated that barbiturate ring is sterically hindered by phenol rings.

Keywords: *Barbituric acid, thymol, quinol, phenlenediamine.*

INTRODUCTION

Barbiturates derived from an acidic basis are barbituric acid **(1)**and are characterized as medium to low acidity compounds withacidic function (7-8) **(2)**. Thesecompounds are not insoluble in water **(3)** and have been preparedto overcome this characteristic Byreacting with sodium ions, which is prepared in the form of salts andbecomes soluble in water **(4)**. Several barbiturates were derivedby substituting the roots in their basic construction, barbituric acid, which scientists agreed to number their atoms **(5)** . Thesederivations include the radical substitution of ethels where hydrogen atoms on carbon 5 resulted in the discovery of the barbiton compound **(6)**. Thereplacement of a vinyl root by thelocation of one of the ethel radicals on carbon 5 (in thebarbiton compound) led to the discovery of phenobarbeton,which is characterized as antimicrobial **(7)** and muscle dysfunction **(8)**. Replace the sulfur element with the oxygenelement on carbon 2 and replace the side chain with the place of one of the ethyl radicals on carbon 5 (in the barbiton compound), resulting in the thiopantone compound **(9)** . The radical replacement of the instance of thetwo hydrogen atoms associated with the azotone 1, 3 and the replacement of cyclohexanyl and the place of one of the ethyl radicals on carbon number 5 resulted in the acquisition ofsodium hexoparbeton **(10)**. Thelatter two have the fastest impact,a group called azomethine (C = N-) **(12 - 14)**. Also, shiff bases derived from aldehyde condensation with primary amines are called al-deamins. In the so-called shiff bases derived from the condensation of ketones with the primary amines are calledal-katamines **(15)**. The stability ofshiff bases depends on the type ofamine and the type of aldehyde orketone used. The bases of the shiffprepared from the aromatic ketone and the aromatic amine arethe most stable between the shiff bases. This is due to increased stability by resonance **(16)**. Azumethin dyes are of great importance and wide use in industries Paper, colored reagents for food and cosmetics **(17-21)**. Azumethin compounds are alsobioactive, used as antimicrobialagents, cancer (8) and others **(22- 25)**.

Methods of work

All compounds were purified by re-crystallization followed by thin layerchromatography and modern spectral techniques. As formelting points, it was measuredusing Staurat MP / MP3. Infrared ie, rapid anesthesia and short impact duration **(11)**. Schiff bases spectra were recorded using a spectrometer (Shimadzu FT-IR8400 S) with a potassium bromidetablet. Absorption spectra were measured in ethanol usingspectroscopy (Shimadzu UV-Vis.1600) at Qadisiyah University - Faculty of Education. The proton NMR spectrum was taken using aBRUKER (300 MHZ) spectrometer in Jordan - Al-Bayt University. Chromatography wasmeasured using Silica Gel TLC plates60 F_{250}.

Methods of Preparation (26-28)

The general method for - preparing the base of azomethin

In R.B.flask (100 ml), put 0.02 mlof PYRIMIDINEderivative and add 25 mL of pure ethanol and then (1 ml)gla. acetic acid, and gradually add (0.06 mol) aromaticamine with (20 ml) pure ethanol and then the mixture reflux for(2hr.) The reaction was followed by chromatography of the thin layer. After heating, the reaction mixture was cooled, the precipitate was then filtered and dried and then recrystallized using ethanol.

The general way to prepare azopigments

Preparation of diazione salt sol.

In a glass baker, prepare a solutionconsisting of 10 mL cooled waterand 10 mL concentratedhydrochloric acid and with continuous stirring (0.02 mL) of the prepared shiff base in the firstpart (A) with cooling in the ice bath (0-5) M, then add to it a coolant solution consisting of (0.06 mol) sodium nitrite + (5 ml)water.

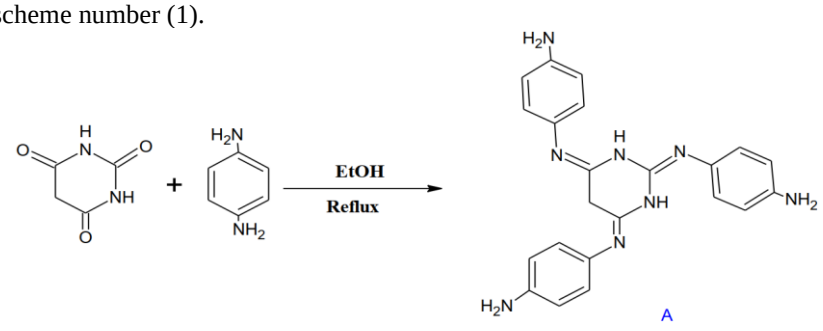
In a second glass baker and - within the ice bath, a solution consisting of dissolving (0.06mol) phenolic compound with (15ml) sodium hydroxide solution (10%).

After continuous stirring in the icebath, add the diazonium salt solution and drops to the couplingsolution. After the addition of themixture, stir the reaction mixture for 15 minutes in the ice bath. Thedeposited precipitate is washed with water and then recrystallizedusing ethanol.

Results and discussion (29-34)

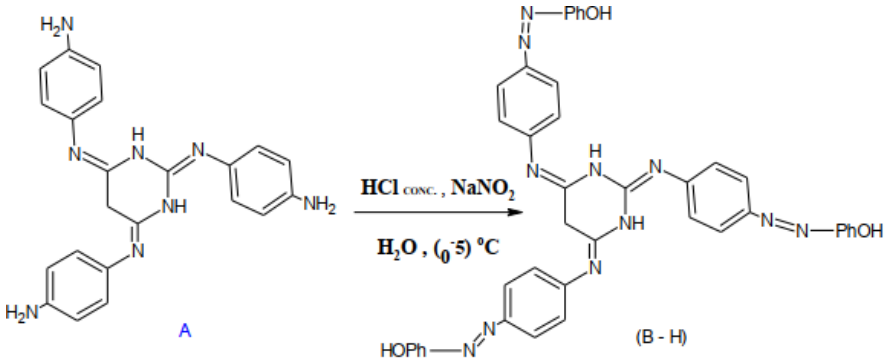
This research included two steps:

The first step was to prepare a newshiff base (A) by reacting the condensation between barbituricacid and the 1,4-phenylene diamine compound, scheme number (1).



Scheme (1)

The second step involved the preparation of new azo dyes through the interaction of shigff base prepared in the first step using diazotization reaction with several phenolic compounds(**scheme** 2). Eight new azotecin derivatives were obtained (COMP.: A-H). Table (1)
represents all physical properties of prepared derivatives. Table (2)represents all the spectral properties of the prepared. compounds (18). Spectra FT-IRshows in Figures ((A - H))



PhOH = PHENOL, 1-Naphthol, 2-Naphthol, Quinol, Resorcinol, 2-aminophenol, thymol).

scheme (2)

Table (1): Physical properties of prepared derivatives (L:Light , D:Dark)

Com.	Phenol	M.Str.	M.wt.(g.mol^{-1})	Yield (g , %)	M.P.(°C)	Color
A	-------	$C_{22}H_{22}N_8$	398.39	(0.3 ,80)	190-192	D.Orang
B	phenol	$C_{40}H_{31}N_{11}O_3$	713.74	)0.4 , 60)	205-206	yellow
C	1-Naphthol	$C_{52}H_{37}N_{11}O_3$	863.92	(0.5 ,70)	257-258	L. yello.
D	2-Naphthol	$C_{52}H_{37}N_{11}O_3$	863.92	(0.6 , 68)	271-273	Orange
E	Quinol	$C_{40}H_{31}N_{11}O_6$	761.74	(0.4 , 58)	232-234	Brown
F	Resorcinol	$C_{40}H_{31}N_{11}O_6$	761.74	(0.4 , 65)	230-232	D.yello.
G	2-Aminophenol	$C_{40}H_{34}N_{14}O_3$	758.78	(0.3 , 55)	240-241	L.orang.
H	Thymol	$C_{52}H_{55}N_{11}O_3$	882.06	(0.2 , 50)	265-267	D.brow.

Table (2): Spectral properties of prepared derivatives

Com.	Phenol	λmax EtOH	FT-IR(cm^{-1}) KBr disk				
			- NH	-C=N	N=N	C–O	-OH ring
A	-------	-------	3373	1635	-------	1284	-------
B	phenol	273	3345	1631	1523	1290	1474
C	1-Naphthol	288	3362	1614	1522	1294	1478
D	2-Naphthol	290	3359	1618	1518	1293	1476
E	Quinol	275	3387	1616	1522	1291	1475
F	Resorcinol	278	3395	1617	1524	1294	1476
G	2-Aminophenol	295	3372	1620	1526	1296	1480
H	Thymol	310	3422	1623	1530	1298	1481

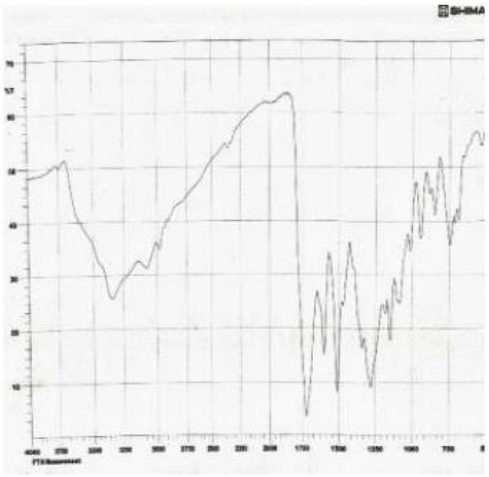


Figure. A

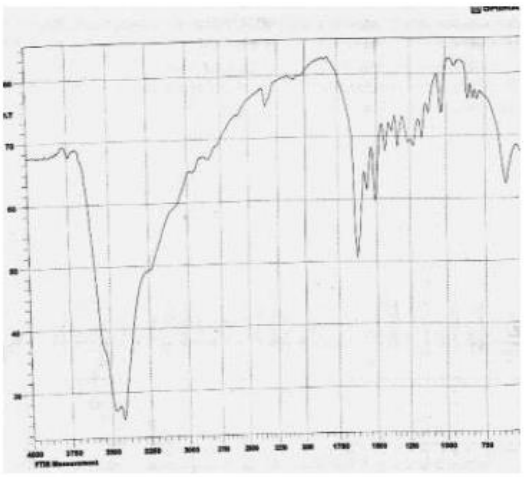


Figure.B

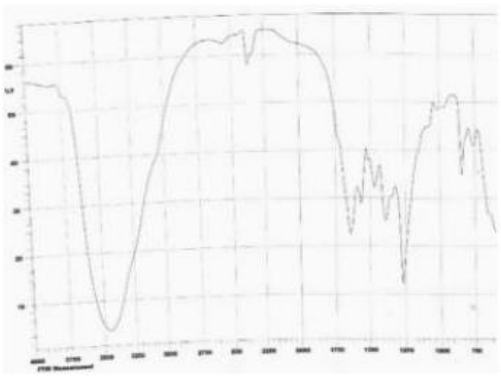


Figure. C

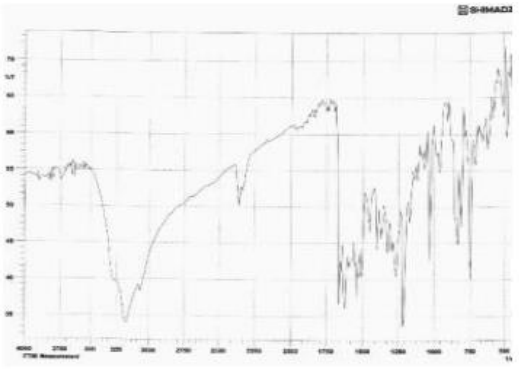


Figure. D

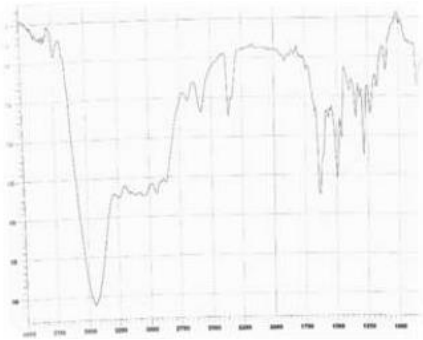


Figure. E

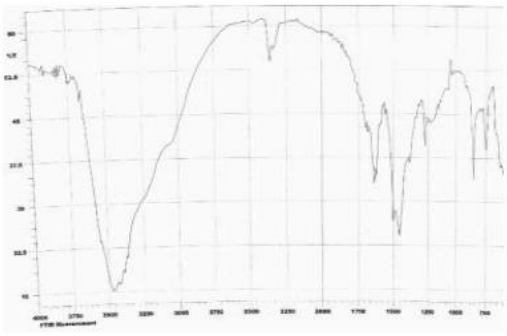


Figure. F

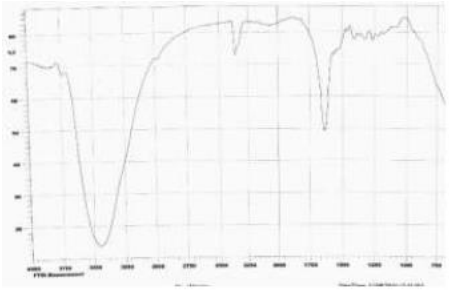


Figure. H

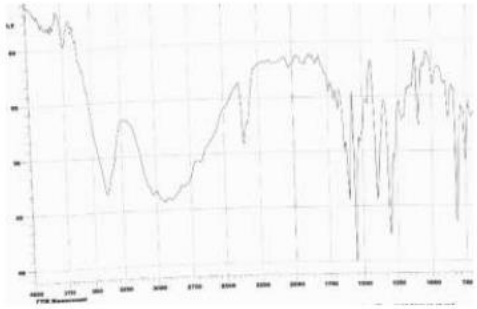


Figure. G

Spectrometry (^{1}H-NMR) of prepared derivatives

^{1}H NMR (300MHz, CDCl3, δ / ppm):

Comp.((A)) : 2.96 (d, 2 H, *J* = 14.8 Hz), 3.59 (d, 2 H, *J* = 14.8 Hz), 6.98 (m, 7 H), 7.06 (s, 5 H), 7.17 (m, 7 H).

COMP.((B)) : 3.31 (s, 2 H), 6.96-7.03 (m, 8 H), 7.32 (m, 8 H), 7.50 (q, 7 H, *J* = 6.4 Hz), 7.60 (dd, 7 H, *J* = 7.0, 1.7 Hz).

COMP.((C)) : 3.29 (s, 2 H), 6.96 (dd, 3 H, *J* = 8.6, 1.9 Hz), 7.22 (m, 7 H), 7.50-7.77 (m, 18 H), 7.81-7.88 (m, 3 H), 8.18-8.27 (m, 3 H).

COMP.((D)) : 3.29 (s, 2 H), 6.98 (d, 2 H, *J* = 8.8 Hz), 7.04 (d, 1 H, *J* = 8.6 Hz), 7.22 (m, 7 H), 7.50-7.70 (m, 15 H), 7.76 (dd, 1 H, *J* = 8.2, 1.6 Hz), 7.86- 8.00 (m, 8 H), 8.11 (dt, 1 H, *J* = 7.8, 2.1 Hz).

COMP.((E)) : 3.23 (s, 2 H), 6.45-6.48 (m, 4 H), 6.83-6.87 (m, 4 H), 7.23 (m, 3 H), 7.31 (s, 11 H), 7.44-7.50 (m, 4 H), 7.67 (d, 3 H, *J* = 8.1 Hz).

COMP.((F)) : 3.08 (d, 1 H, *J* = 15.3 Hz), 3.38 (d, 1 H, *J* = 15.3 Hz), 6.45-6.48 (m, 4 H), 6.83-6.87 (m, 4 H), 7.23 (m, 3 H), 7.31 (s, 11 H), 7.44-7.50 (m, 4 H), 7.67 (d, 3 H, *J* = 8.1 Hz) .

COMP.((G)) : δ 3.21 (s, 3 H), 6.48 (d, 1 H, *J* = 1.8 Hz), 6.55 (d, 3 H, *J* = 1.1 Hz), 6.68-6.71 (m, 4 H), 7.15 (m, 6 H), 7.21-7.31 (m, 12 H), 7.54 (d, 4 H, *J* = 8.2 Hz).

COMP.((H)) : 1.32 (d, 20 H, *J* = 6.8 Hz), 2.08 (s, 3 H), 2.13 (s, 6 H), 3.27 (s, 2 H), 3.38 (h, 3 H, *J* = 7.1 Hz), 6.68 (s, 2 H), 6.80 (s, 1 H), 7.20-7.29 (m, 7 H), 7.46-7.51 (m, 9 H), 7.63 (s, 1 H) .

The NMR spectrum of theazoketimines indicates that there are several overlapping electronic environments of the prepared compounds due to the diversity ofthe active groups found in these compounds in that they are driving or drawing aggregates(such as azomethane, hydroxyl,amine and alkyl groups), in addition to the abundance and diversity of hydrogen atoms (6.60ppm) refers to the adjacent protons of the base aromatic ring,whereas the signal (6.80 ppm) belongs to the opposite protons ofthe aromatic compound. The opposite protons of the aromatic amine compound, close to the azomethin group, show a clear signal with double bursts of 7.81 ppm. For the latter, they are due tothe opposite protons of the base aromatic ring, especially near the fivering.

For the phenol compound, one ofthe most significant signs of the characteristic resonance characteristic is the signal

(6.99 ppm) of the corresponding phenolring protons, which at the same time are protons adjacent to the other phenol loop protons, causing double and double fissures. As for the naphthol dye, the most important signals are measured between the extendedvalues (ppm 7.09 - 8.03), which are related to the protons of the alpha-naphthol ring, which are close to the hydroxyl driving group and the torso-tzo group, Hydrogen atoms. As forazumethane and pyrethylene, the presence of the high-densityelectron groups creates electronicenvironments that obscure or reduce the appearance of signals and thus reduce their measuredvalues or observations. This is observed for these compounds,

Conclusions

The main objective of thisresearch is to prepare newazotecins containing several phenolic derivatives using one of the important organic reactions,which is the reaction of azuna.The classical and modern techniques were used in the diagnosis of prepared compoundssuch as melting grades, chromatography, Ultraviolet- the most important of which are the measured values 7.17 - 6.91 ppm), which is due to the proton ring between the hydroxyl drivinggroups. The characteristic andphenolic value of the phenolic compound is a signal between 7.18 - 6.80 ppm, which comesfrom protons confined between the iso group and the amino and hydroxyl groups. The most recentof these thymol has several distinctive signs, the mostimportant of which is the signal (3.23 ppm) of proton, the isopropyl group, which is affectedby the high electronic environment of the two kinetic groups, as well as the signal (1.96ppm) of the three methyl groups of the thymol. (Ppm 1.18). The signal (6.99 ppm) belongs to the thymol group, which is bound to the methyl and hydroxylgroups.

visual radiation, proton spectroscopy and NMRspectroscopy. The percentages of derived derivatives approximatelygood. We hope that our research will be done in the form of new azotecin dyes used in some industrial and applied fields such as dyes, various medicines, cosmetics, colored reagents andanalytical chemistry guides .

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