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# Synthesis Of Phenol Formaldehyde Resin By Mannich Bases And Study Some Their Applications Industrial And Biologycal

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**Abstract:**

In this work, new phenol formaldehyde resin were prepared by Mannich bases functional groups. The work included two parts ; part one syntheses of Mannich bases monomers formed by the condensation reaction of aromatic aldehyde (P-hydroxy benzaldehyde) with primary amines such as (4-amino antipyrene, 2-aminobenzothiazole, sulfamethaxazole, Metoclopromide and trimethoprim) with secondary amine Piperazine have been synthesized. Then part two included synthesis of phenol formaldehyde resin containing Mannich bases by condensation Mannich bases which prepared in part one and formaldehyde and phenol. These phenol formaldehyde resin were characterized through (FT-IR) and($^1$H-NMR) spectroscopy so study the biological activity of some of the synthesized compounds .

**Keywords:** -Piperazine , phenol formaldehyde, resin, polymerization, Mannich bases.

**Introduction:**

One of the highly effective resins is phenol formaldehyde (P.F.) resin, which can be obtained from the reaction of phenol with formaldehyde. This resin has wide uses in the industrial field, especially the formation of plastics and resin adhesives. [2]. The characteristic of ( P.F.) resin clued high mechanical; thermal and weather stability [3]. So, the lower processingrate and required higher curing temperature compared to other thermosetting adhesives limit the application of (P.F.) resins for use their in imbibitions and adhesives [4].

In this paper a new series of phenol formaldehyde, resin was prepared by reaction phenol and formaldehyde with Mannich bases, which have gained importance due to their application pharmaceutical chemistry [5]. They have been studied intensively mainly due to its application in organic synthesis particularly for preparing dyes, industrial , pharmaceutical and antimicrobial such as antibacterial [6], anticancer [7], anti-inflammatory[8] and anticonvulsant [9-10],so secondary amine used to prepared Mannich bases is piprazine. Piperazine is a unique heterocyclic constituent of several biological active compounds. The polar nitrogen atoms in the Piperazine ring considered bioactive molecule and enhance

favorable interaction with macromolecules, Piperazine residue containing compounds have been reported to have antibacterial activity [11-13]. The medicinal value of piperazine derivatives is significant among various heterocyclic, as they are found to possess various biological activities. Moreover, several bis (heteroaryl) piperazine derivatives (BHAP) have been introduced as potent anti HIV drugs [14-16].

**Chemicals and Methods:**

In this work the chemicals used were sourced from (Sigma, BDH, Merch, Aldrich ND Fluka), so are used without from purification.SMP3 uses digital Stuart Scientific to record the Melting points apparatus and are uncorrected. (FT-IR) spectrum was registered in (SHIMADZU) (FT-IR-8400) Fourier transform infrared spectrophotometer in the (4000-6000) $cm^{-1}$ spectral range internal reference measurements.so($^1$H-NMR) spectra were recorded on Bruker (500 MHz ) instrument using (DMSO-d6 ) and (TMS) which is internal reference measurement were made at chemistry department in Al albayt University , Jordan.

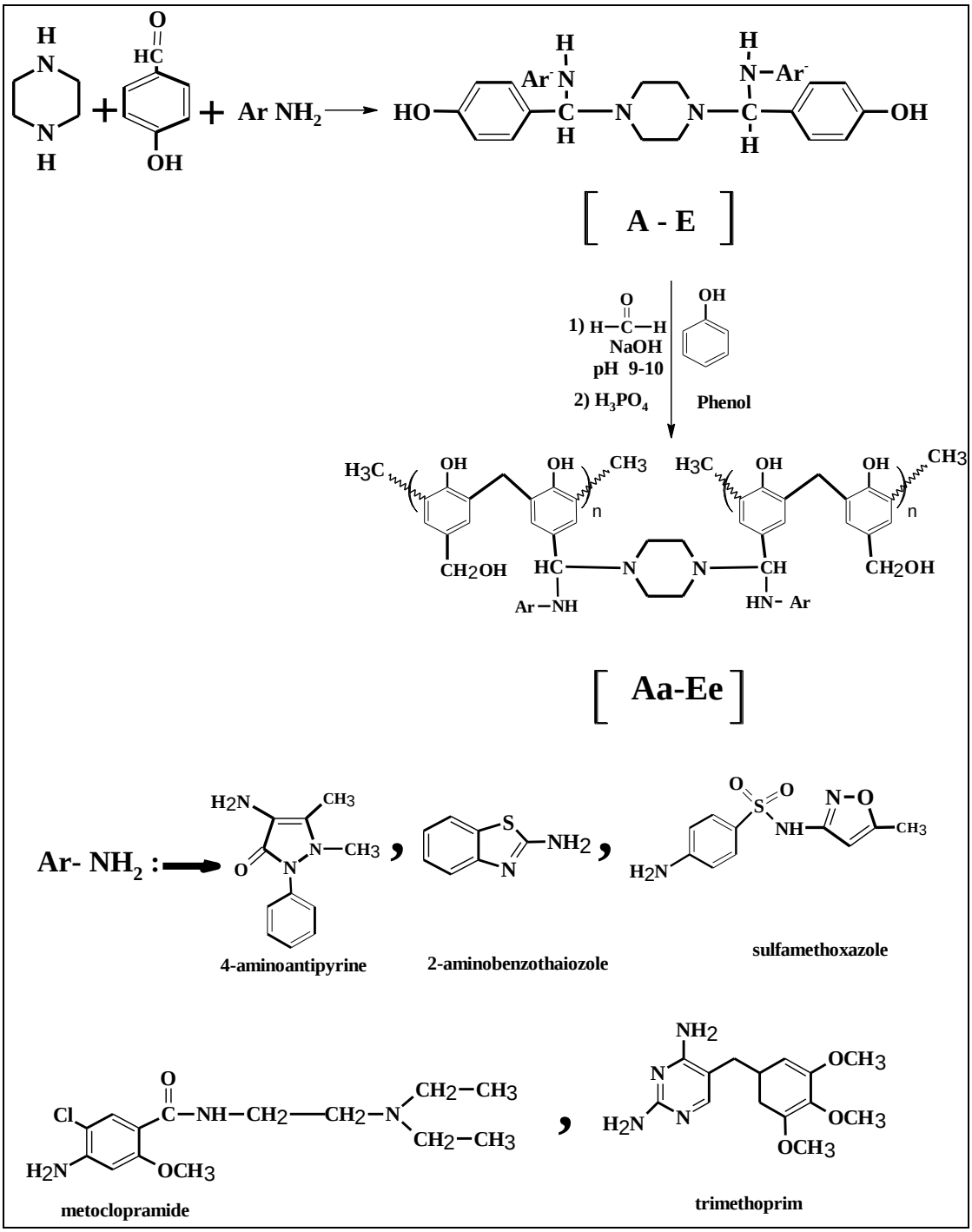
**Method for the synthesis of Mannich bases [5]:**

In round bottom flask was placed solution of piprazine (0.001mol ) in 10 ml of DMF with (0.002 mol) of different primary amines such as (4-amino antipyrene, 2-aminobenzothiazole, sulfamethaxazole, Metoclopromide and trimethoprim) and P-hydroxy benzaldehyde ( 0.02 mol) has been refluxed for (5hr). Solvent used was evaporated then residue poured in ice water with stirring.The precipitate was recrystallized from DMSO after filtering. The physical properties for products (A-E) in table (1).

**General methods for the synthesis of Phenol- Formaldehyde [3]:**

The batch polymerization process was used to prepare phenol-formaldehyde resin with a molar ratio (1: 2: 2) of phenol and formaldehyde by adding 6% of the catalyst on a total origan.

Phenol was mixed in flask with formaldehyde and prepared Mannich bases in the presence of the catalyst.The heater is switched off when the temperature of the mixture rises to (70) ° C, and to complete the polymerization reaction, the mixture is reheated to 90 ° C to restore the resulting heat and reside in ( 93-95 )ºC for 1 hr were synthesized with the same procedure. The physical properties of resins (Aa - Ee) are listed in table (2).

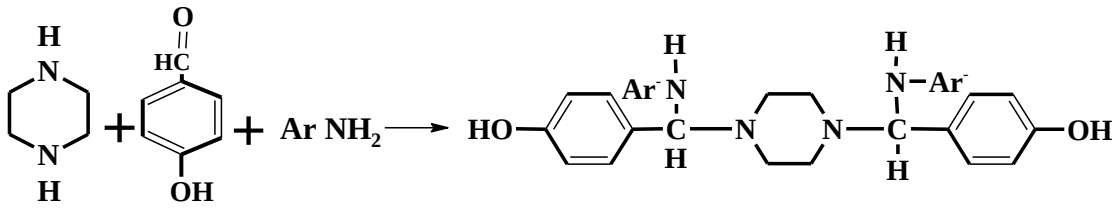



**Scheme (1)**

**Result and Discussion:**

In this study comparison the synthesis of the phenol formaldehyde resin functionalized by Mannich bases have been functional groups.

This work included four parts, part one: novel Mannich bases have been synthesized by reaction between piprazine, parahydroxy benzaldehyde and different primary amine (A –E) which evaluated them for antifungal activity.



The productstructures of all the newly synthesized compounds were confirmed from during suitable spectral technique as in ($^1$H-NMR and FT-IR).

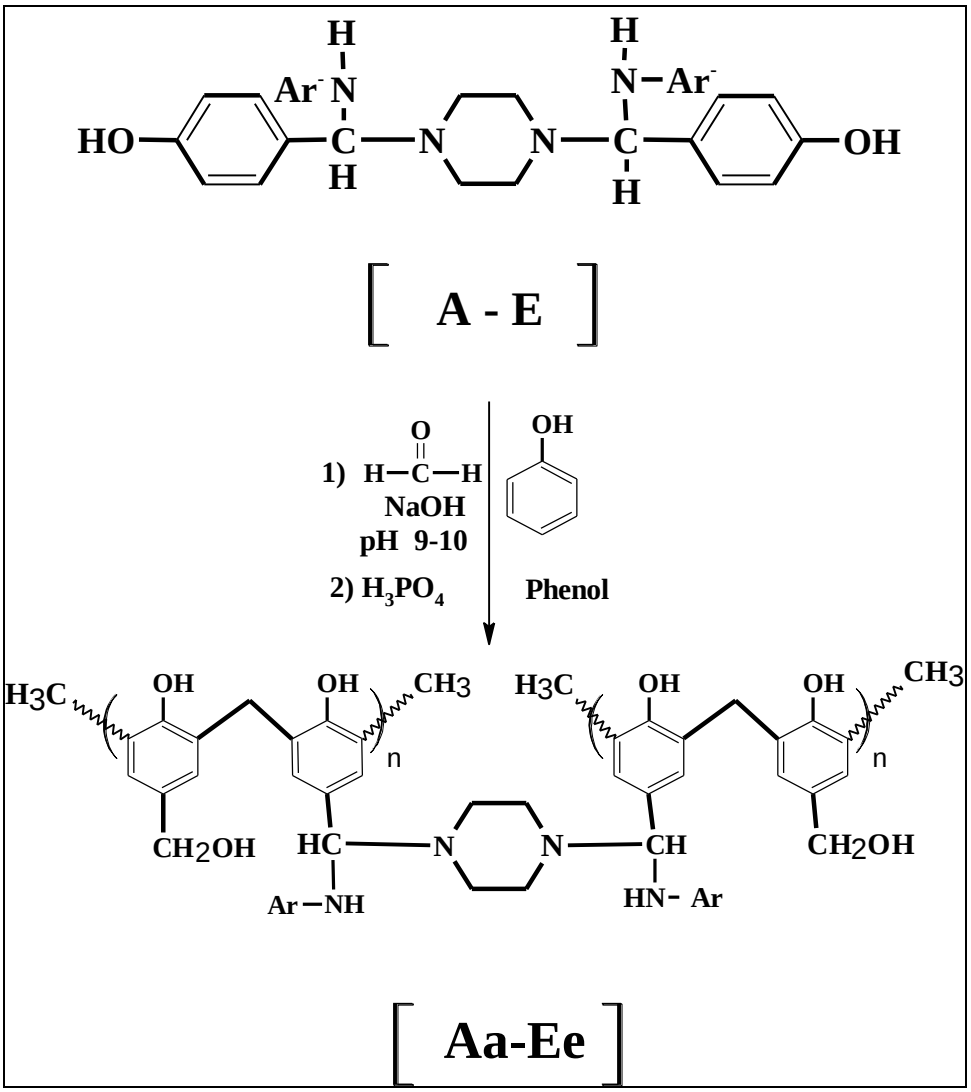
In FT-IR spectrum for compound (C ) figure (1) appear absorption band of (3240)cm$^{-1}$ return to υ (N-H) the amide , other bands in (3009, 2758-2870,1577 and 3437 ) cm$^{-1}$ which are return to υ (C-H) arom., υ (C-H) aliph., υ (C=N) and υ (O-H) of phenol and υ (C-N) respectively. So, the FT-IR spectrum of compound (D) figure (2) showed absorption disappearance of υ ($NH_2$) for amine appearance of band at (3402) cm$^{-1}$ due to υ (O-H), another bands appeared in (1600, 3221,1477, 2970 and 2800-2877) cm$^{-1}$ whichare return to υ (C=C), υ (N-H), υ (C-N), υ (C-H) aromatic and υ (C-H) aliphatic successively.

During the $^1$H-NMR spectra, the signals of the competent prepared derivatives were verified on the basis of their chemical shifts, multiplication and pairing constant.

($^1$H-NMR) spectrum of compound (B) figure (5) appear signals at phenyl proton δ(7.20 -7.96) ppm. 1 H proton of (NH-C) at δ(6.55) ppm, 2H protons of ($CH_2$-N) were at around δ(4.24) ppm. 1 H proton of (OH) at δ (9.78) ppm, 1 H proton of (CH-N) at δ (0.23) ppm and 4 H protons at (-$CH_2$-$CH_2$-) at δ (3.53-3.85) ppm.
So, $^1$H-NMR spectrum of compound (E), figure ( 7 ) exhibit signals in δ (7.30-7.51) ppm return to aromatic ring protons δ (6.55) ppm return to ($NH_2$), (3.61) due to (O-$CH_3$), (8.06) due to (OH) phenolic group, (6.15) ppm return to (NH-C) and (1.10-1.35) due to 1H protons for (N-CH-N). Also, appeared signals in δ (5.76) ppm belong to (4 H) protons of (-$CH_2$-$CH_2$-).

Part two:

In this work involved phenol formaldehyde (PF) resin (Phenolic chelating polymers) was synthesized via batch polymerization with phenol, formaldehyde and Mannich bases which prepared in part one (A-E) , scheme (1).




The condensation state also affects the structure of the resin, Since the aromatic phenol ring containing ortho and para position, has the ability to condense with formaldehyde, but the position is more related than the position ortho.

The existence ofone para position and two ortho position in an aromatic ring generally could result to a phenol process of (phenol formaldehyde) resin synthesis. The catalysts can make more formaldehyde resin containing especially (ortho) hydroxyl methyl groups. So however in fhormaldehyde or methylol towards phenol (ortho) positions to excess the ratio ortho on para substituted positions bring about more reactive functional groups or more un reacted par a positions in the treatment stage, that may become shorter the treatment time and excess the cross-linking degree for cured (phenol formaldehyde) resin [1,4].

In general the new derivatives for phenol formaldehyde resin was characterized by physical properties, spectroscopic data, tables (1), (2). The FT-IR spectrum of compound (Cc),figure (3) shows bands in ( 2966, 2823, 1612, 3305, 3390 and 1469) $cm^{-1}$ back to υ (C-H) arom., υ (C-H) aliph., υ (C= C), stretching band for υ (N-H), υ (O-H) and υ (C-N). Also compound (Dd), Figure ( 4 ) shows bands at : ( 2966, 2823, 1593, 3245, 3400 and 1512) $cm^{-1}$ due to υ (C-H) arom., υ (C-H) aliph., υ (C= C), υ (N-H), υ (O-H) and υ (C-N)successively.

$^1$H-NMR spectrum of compound (Bb), figure ( 6 ) exhibit signals at δ(9.57) ppm, due to υ (OH) phenolic group, δ (6.90-7.10) ppm return to aromatic ring protons, δ (8.51) ppm return υ (-NH), and δ (3.30-3.71) ppm return to 4H protons for (N-$CH_2$-$CH_2$N). Also appeared signals at δ (4.50-4.78) ppm and at δ (1.30) ppm belong to ($CH_2$-OH) proton and (-$CH_2$-) proton respectively. While $^1$H-NMR spectral data of compound (Ee), figure ( 8 ) showed signals in δ (6.97-7.72) ppm return to arom. ring proton; δ (9.57) ppm, return to (OH) phenolic group, (6.58) ppm return to (-NH), (3.70) ppm return to (O-$CH_3$). So appeared signals at δ (2.18-2.41) ppm belong to (-CH2-) proton and δ(4.50-4.78) ppmbelong to ($CH_2$-OH) proton.

**Table (1) show physical properties of prepared Mannich bases (A-E)**

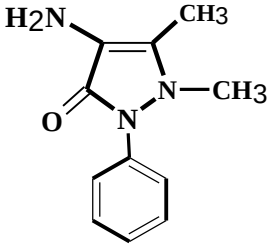
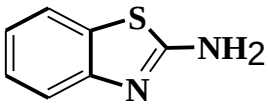
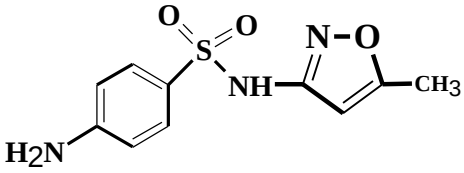
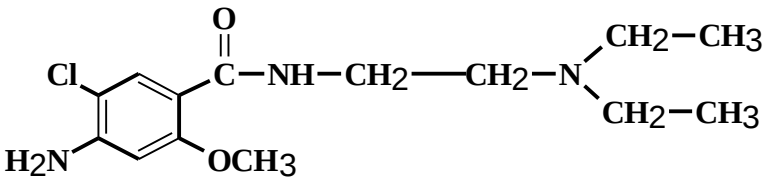
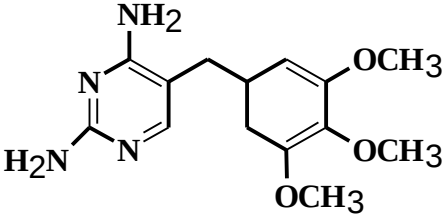
| Comp. No. | Comp. structure | M. P. C° | Color | Yield% | Molecular formula |
|---|---|---|---|---|---|
| A |  **4-aminoantipyrine** | 144-146 | Yellow | 60 | $C_{40}H_{46}N_8O_4$ |
| B |  **2-aminobenzothaiozole** | 170-172 | Faint Yellow | 70 | $C_{32}H_{32}N_6O_2S_5$ |
| C |  **Sulfamethoxazole** | 190-192 | Yellow | 45 | $C_{36}H_{42}N_8O_8S_2$ |
| D |  **Metoclopramide** | 242-244 | Brown | 50 | $C_{46}H_{64}ClN_6O_2$ |
| E |  **Trimethoprim** | 133-135 | Orange | 56 | $C_{46}H_{56}N_{10}O_8$ |

**Table (2) physical properties data of prepared resins(Aa-Ee)**

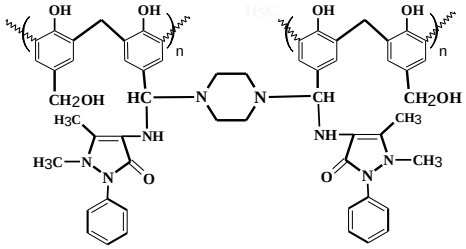
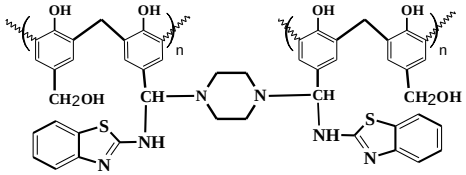
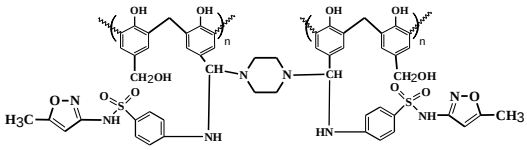
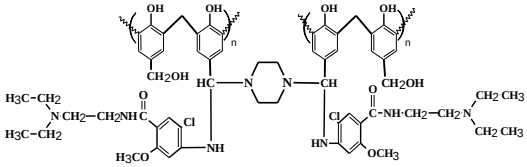
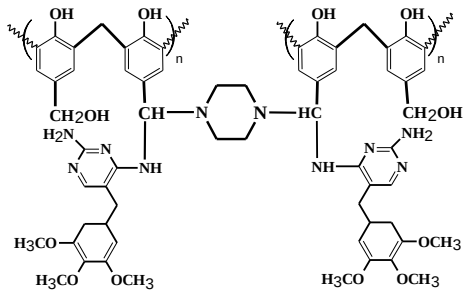
| Comp. No. | Compound structure | Color | Yield% | Soft ting point ºC |
|---|---|---|---|---|
| Aa. |  | Brown | 50 | 235-243 |
| Bb. |  | Dark brown | 65 | 290-305 |
| Cc. |  | Dark yellow | 55 | 282-293 |
| Dd. |  | Dark Brown | 62 | Oily |
| Ee. |  | Dark yellow | 60 | 266-280 |

**Table 3:(FT-IR) spectrum for all product compounds**

| Com. No. | υ C-H arom. $cm^{-1}$ | υ C-H aliph. $cm^{-1}$ | υ C=C $cm^{-1}$ | υ N-H $cm^{-1}$ | υ O-H $cm^{-1}$ | υ C-N $cm^{-1}$ | Others $cm^{-1}$ |
|---|---|---|---|---|---|---|---|
| A. | 3059 | 2910 | 1589 | 3263 | 3471 | 1473 | 1658 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| B. | 3055 | 2819-2970 | 1573 | 3186 | 3305 | 1446 | (C=N) ring 1535 |
| C. | 3008 | 2758-2870 | 1600 | 3240 | 3437 | 1465 | (C=N) ring 1577 (S=O) 1238 |
| D. | 2970 | 2800-2877 | 1631 | 3221 | 3402 | 1477 | (C=O) Amid 1651 |
| E. | 2931-3050 | 2831 | 1593 | 3124 | 3468 | 1452 | (C=N ) 1653 |
| Aa. | 2985 | 2831 | 1593 | 3335 | 3448 | 1477 | (C=O) 1643 |
| Bb. | 2951 | 2893 | 1612 | 3260 | 3398 | 1454 | (C=N) 1643 |
| Cc | 2989 | 2893 | 1612 | 3305 | 3390 | 1469 | (C=N) ring 1643 (S=O) 1273 |
| Dd. | 2966 | 2823 | 1593 | 3245 | 3400 | 1512 | (C=O) amid 1797 |
| Ee. | 3028 | 2835-2918 | 1608 | 3340 | 3444 | 1458 | (C=N) 1639 |

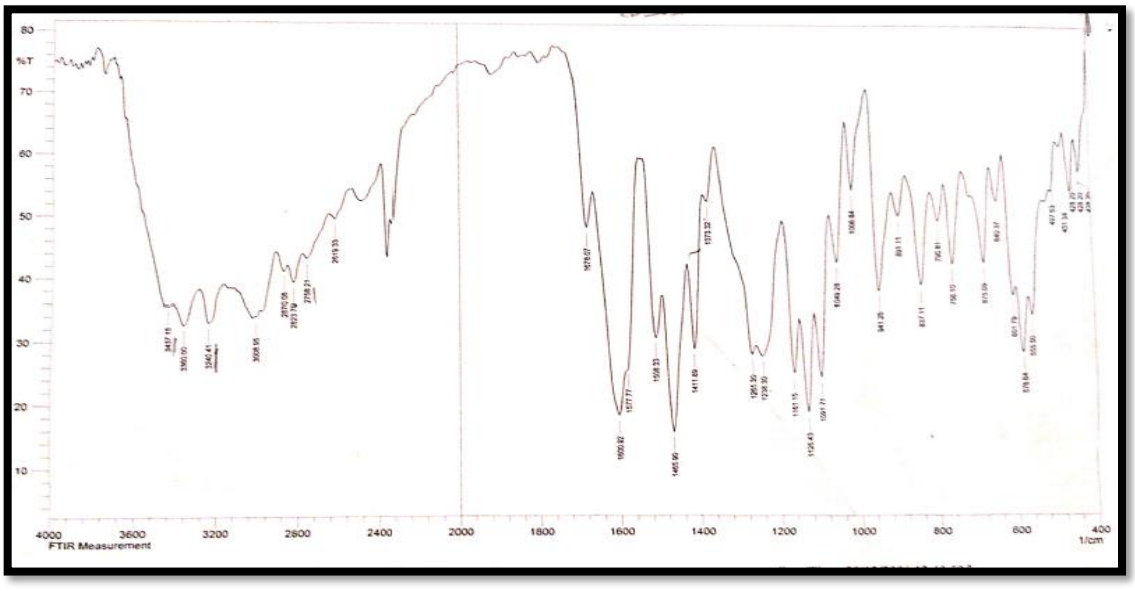


Figure. 1 :show( FT-IR) for prepared compound (C)

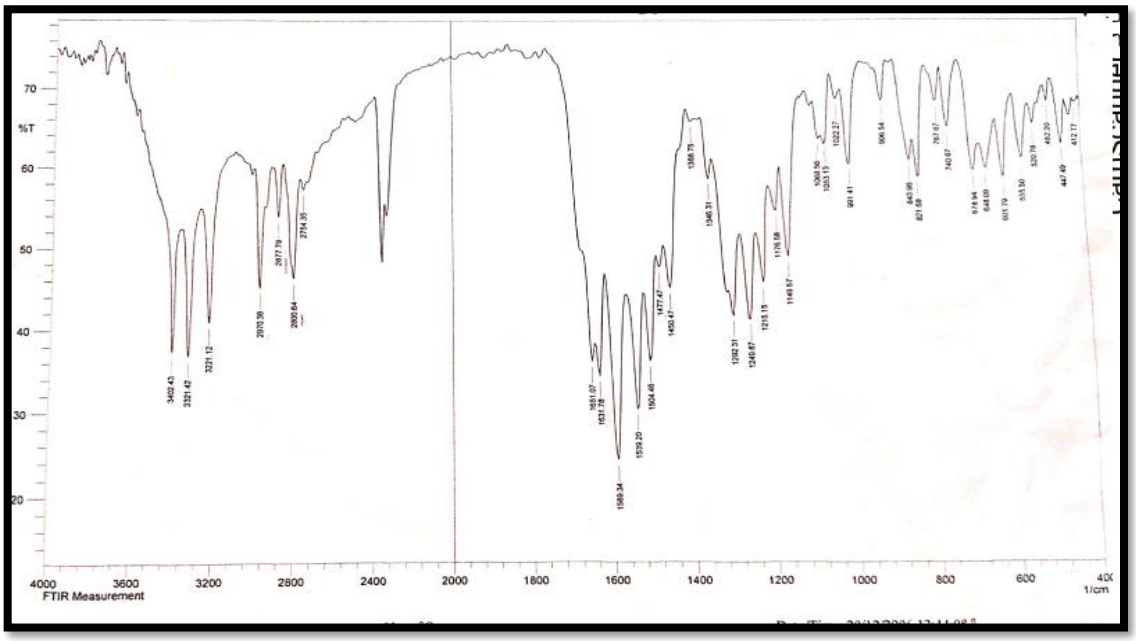



Figure. 2: Show( FT-IR ) for prepared compound (D)

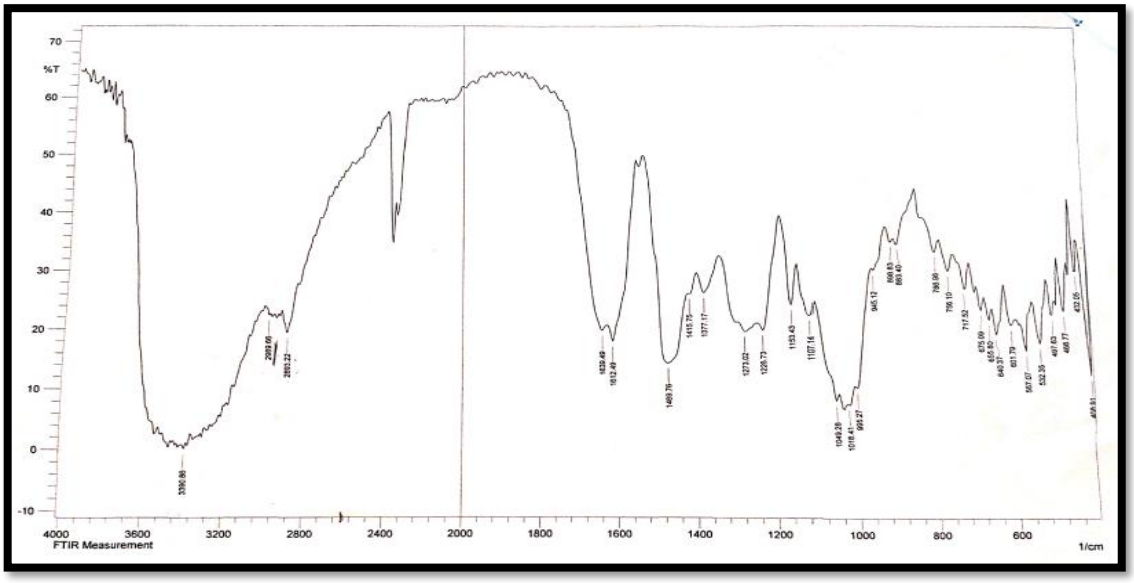



Figure. 3: Show ( FT-IR) for prepared compound (Cc)

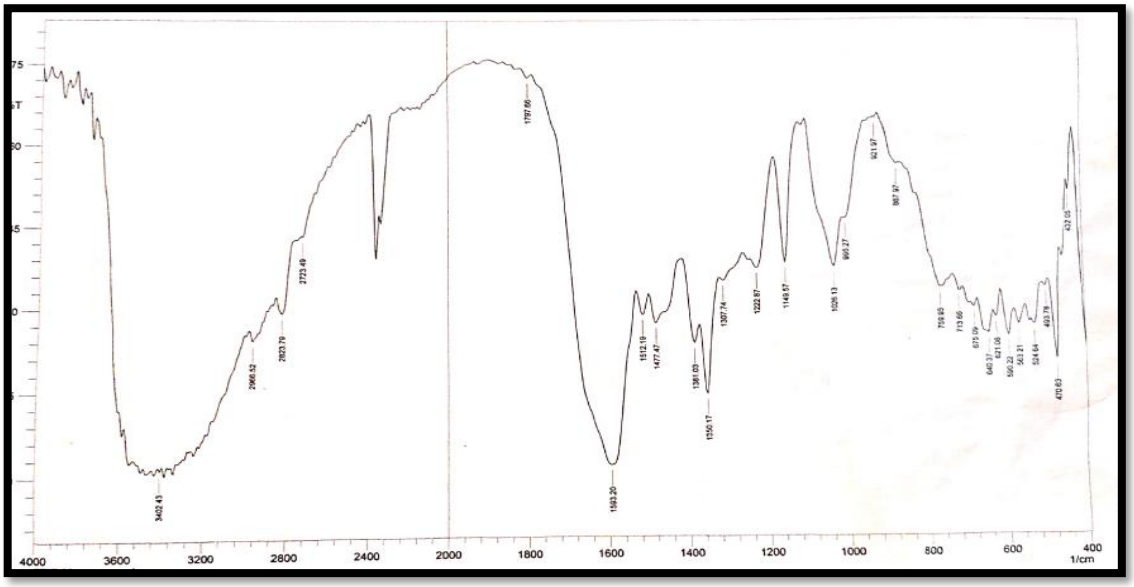



Figure. 4 : Show( FT-IR) for prepared compound (Dd)

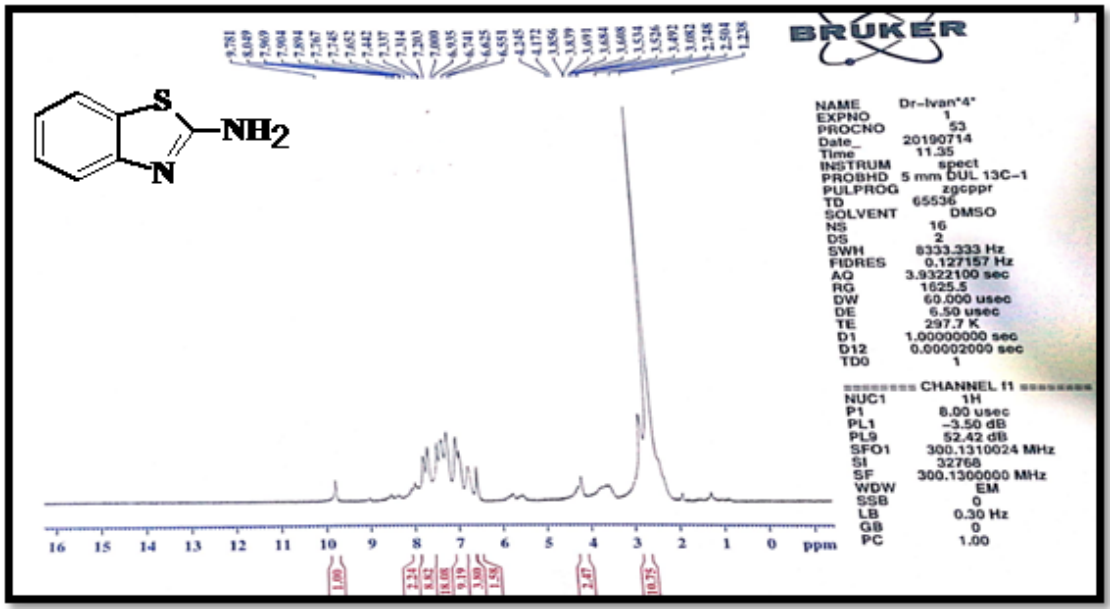



Figure 5 :Show ($^1$H-NMR) spectral for prepared compound (B)

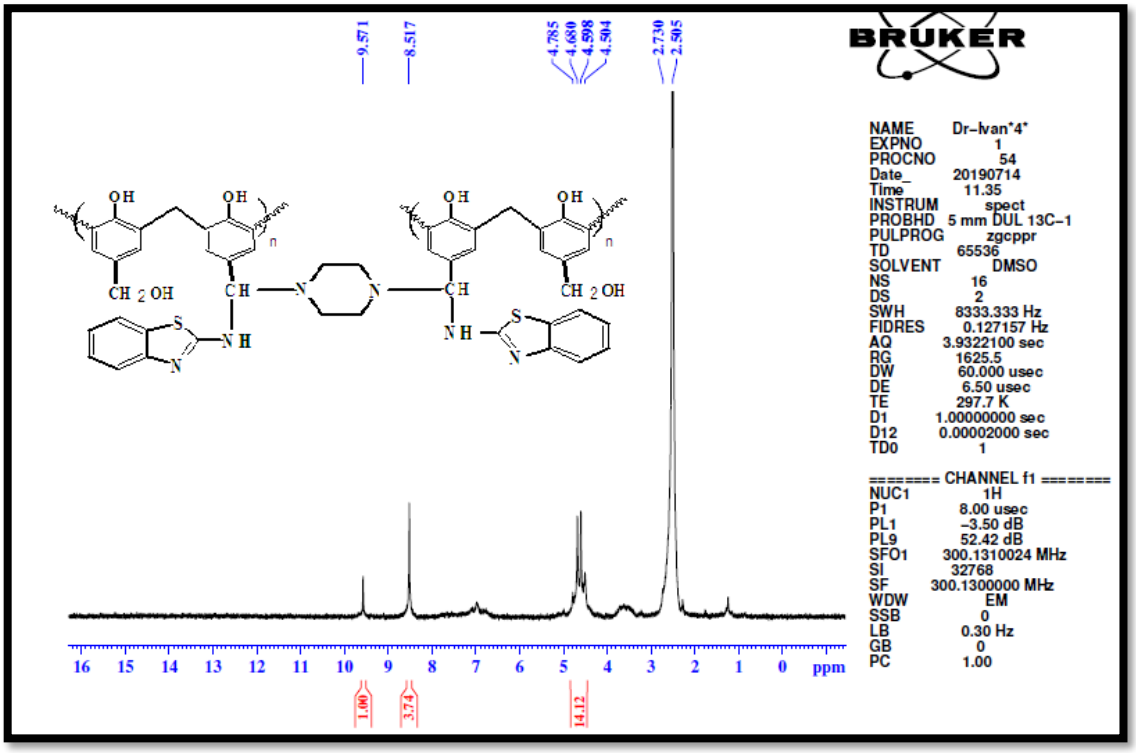



Figure 6: Show($^1$H-NMR) spectral for prepared compound (Bb)

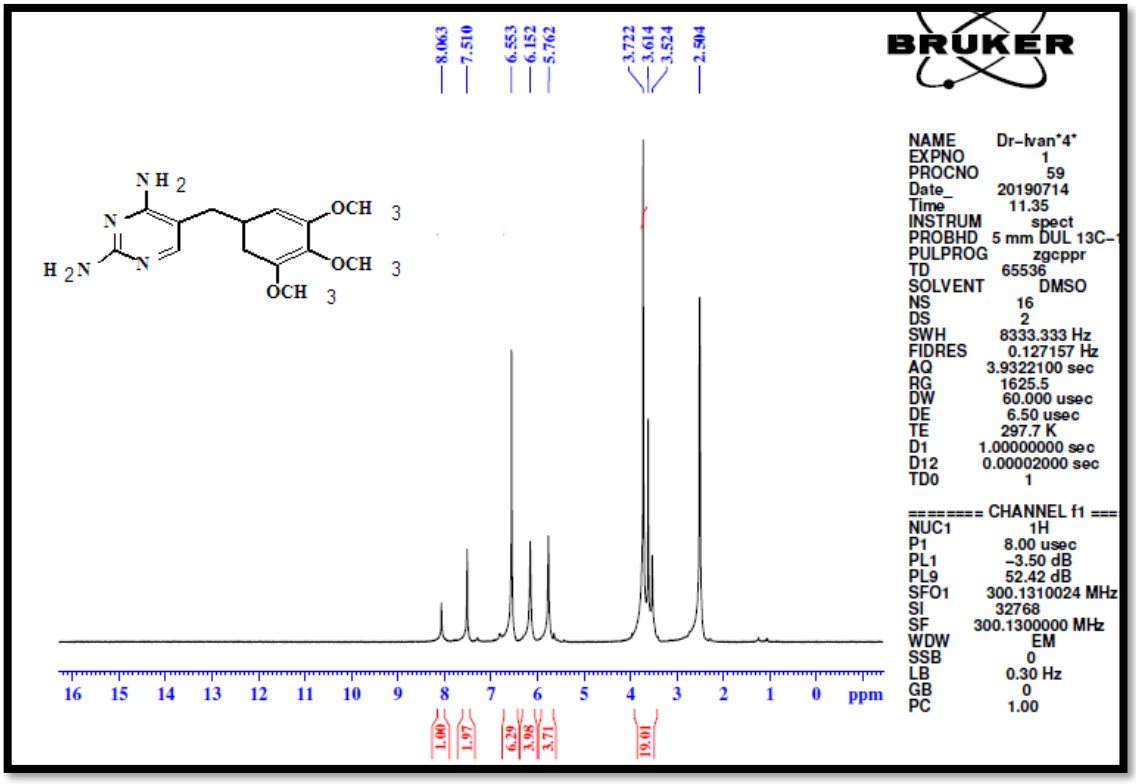



Figure 7 :Show ( $^1$H-NMR) spectral for prepared compound (E)

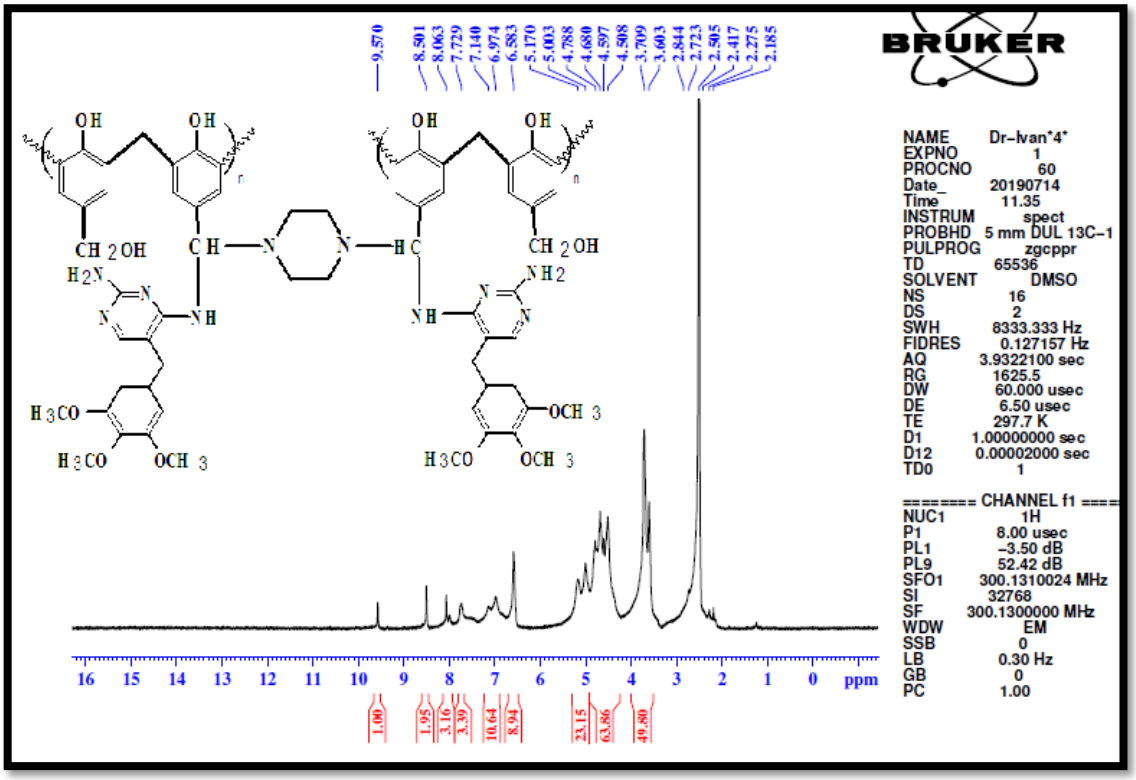



Figure 8: Show ($^1$H-NMR) spectral for prepared compound (Ee)

**Part three**

While part three includes antibacterial activity. The preliminary study of the synthesized compounds to determine their biological effectiveness for future use as pharmaceuticals or drugs by the evaluation of biological activity [17] of some synthesized compounds against two types of bacteria gram positive, namely Staphylococcus aureus, Bacillus subtillus and against gram –negative bacteria namely, Eschericha. Coli. Klebsiella. SPP, Acintobacterbaumannii as well as Rhizosporium summarized in table (4) .

DMSO was used as solvent for all compounds (Mannich bases) and as control. The table (4) showed the efficiency of synthesized compounds against certain species without others, different inhibition zones size against tested bacteria strains was observed, the result showed that synthesized compounds have high activity against gram positive and gram negative bacteria for compound (Ee) better than from all the compound which products or compound (Ee) exhibited excellent and highest activity against all kinds of bacteria as well as Rhizosporium and that due to the activity of resin compounds. Inhibition zones resulted from all tested compounds which shown in the table (4).

**Table (4) Antimicrobial and antifungal inhibition zone (mm) of some of the synthesized compounds**

| No.of lab | Comp. | Inhibition zone (mm) at 10 mg/ml against | | | | |
|---|---|---|---|---|---|---|
| | | Gram positive | | Gram negative | | Rhizo. |
| | | Staphylococcus aureus | Bacillus subtillus | Eschericha. Coli. | Klebsiella SPP. | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 4 | B | 13 | 21 | 27 | 14 | 12 |
| 1 | D | 16 | -Ve | 27 | 12 | 12 |
| 15 | E | 26 | 14 | 24 | 15 | 15 |
| 7 | Aa | 21 | -Ve | 22 | 15 | 12 |
| 5 | Bb | 18 | 15 | 25 | -Ve | 15 |
| 3 | Cc | 17 | 14 | 27 | -Ve | 11 |
| 2 | Dd | 15 | -Ve | 21 | 14 | 13 |
| 6 | Ee | 15 | -Ve | 35 | 17 | 13 |
| Piperazine | Pip. | 15 | 14 | 15 | 14 | 12 |

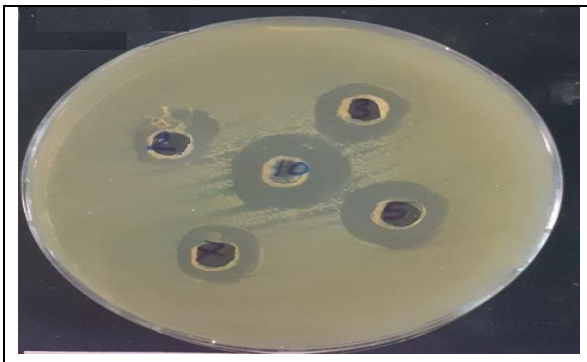


Fig. 9: Effect of comp. (2,3,7,6,5) in (Staphylococcus aureus)

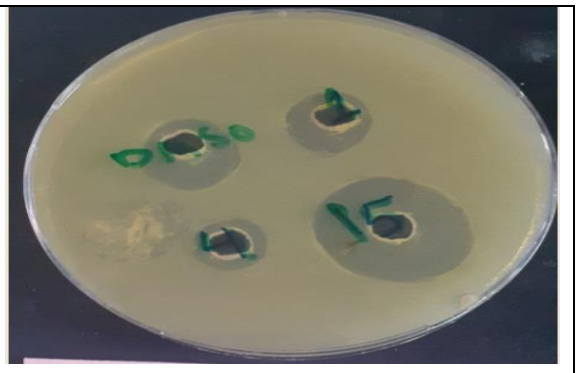



Fig10: Effect of comp. (1,4,15) in (Staphylococcus aureus)

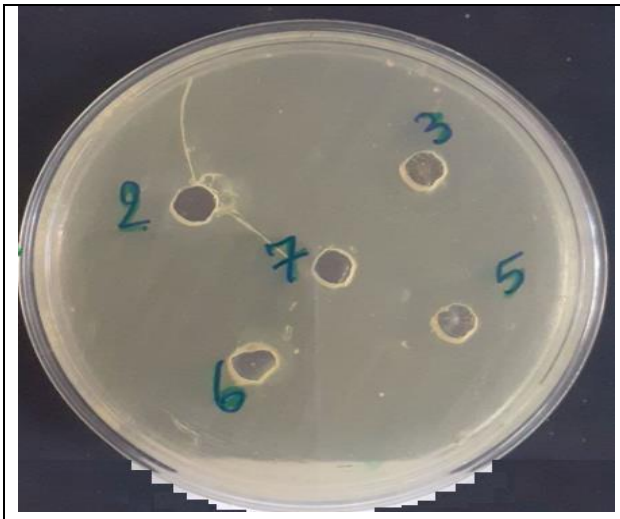



Fig. 11: Effect of comp. (2,3,6,7,5) in ( Bacillus subtillus)


Fig. 12: Effect of comp. (1,4,15) in ( Bacillus subtillus)

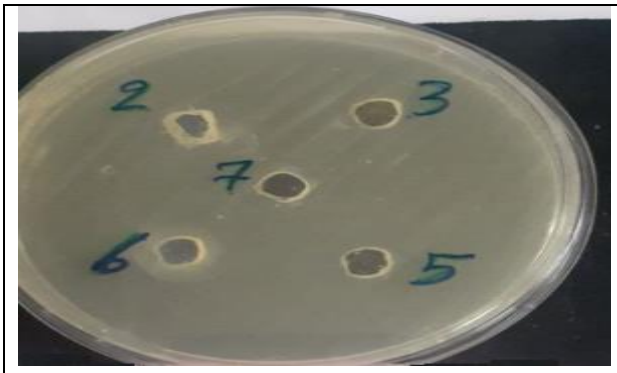



Fig. 13: Effect of comp. (2,3,6,7,5) in (Eschericha. Coli.)

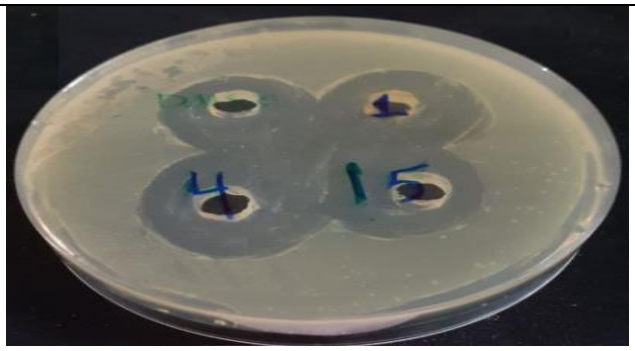



Fig.14:: Effect of comp. (1,4,15) in (Eschericha. Coli.)

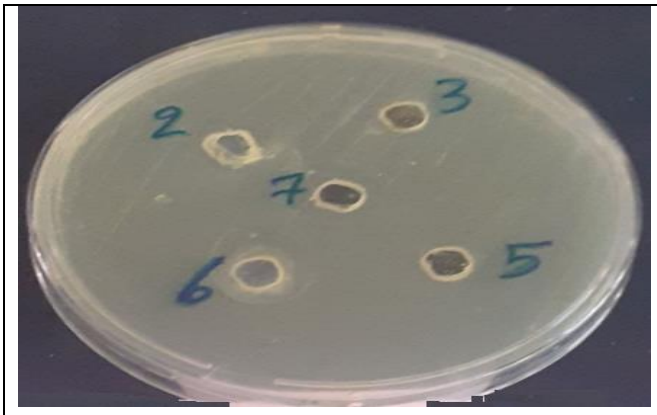



Fig. 15: Effect of comp. (2,3,6,7,5) in (Klebsiella SPP.)

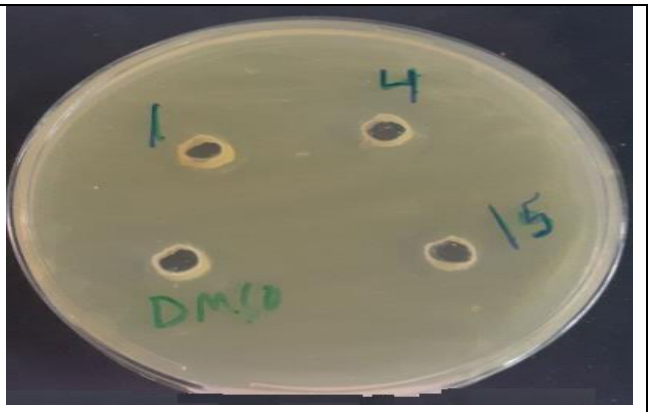



Fig. 16: Effect of comp. (1,4,15) in (Klebsiella SPP.)

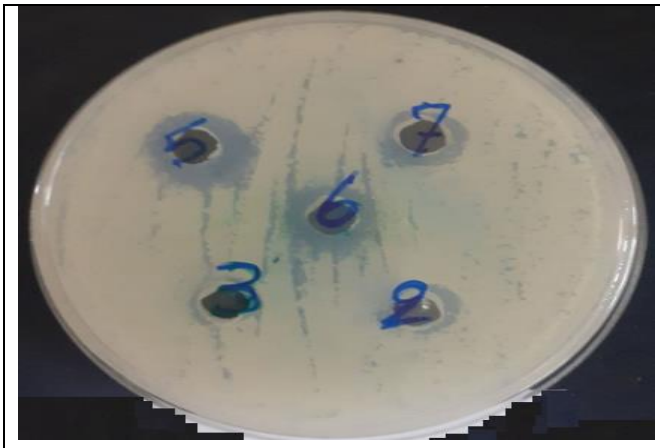



Fig. 17:: Effect of comp. (2,3,6,7,5) in (Rhizo.)


Fig. 18: Effect of comp. (1,4,15) in (Rhizo.)

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