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Synthesis, Spectral Investigation and Microbial Studying of Pyridine-Heterocyclic Compounds

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Abstract: Pyridine is one of the natural compounds that it builds upon in the formation of other chemical compounds in a number of applied industrial fields such as agricultural chemistry and the pharmaceutical industry. Pyridine is used in industry as a chemical solvent and reagent; And also in DNA synthesis in the laboratory. Historically, pyridine was obtained from coal tar and as a by-product of the coal gasification process; However, the increased demand for it has led to the development of synthetic reactions of simple compounds such as acetaldehyde and ammonia. Annually, more than 20 thousand tons of the compound are produced worldwide. Series of Pyridine –heterocyclic derivatives were prepared via cyclization reaction and condensation reaction, then identification all prepared new compounds via several techniques (FT.IR, H.NMR, Mass)– spectrophotometric, other physical and chemical properties, with microbial studying for all new prepared pyridyl derivatives.

Keywords: Pyridine, Thiazole, Imidazole, Thiadiazole, Oxadiazole, Triazole, Antimicrobial, Heterocyclic, Phenylene Diamine.

1. INTRODUCTION

Pyridine (Py) is an organic compound with the chemical formula C5H5N, which is a heterocyclic aromatic compounds[(1-3)]. The pyridine structure consists of an unsaturated hexagonal ring containing an atom of nitrogen, and this ring is found in the structure of a number of important compounds, including azines and others such as niacin, pyridoxinocinisoniazid, and nicotine. Pyridine is a precursor to form other chemical compounds in a number of applied industrial fields such as agricultural chemistry and pharmaceutical industry[(4-8)]. Pyridine is used in industry as a chemical solvent and reagent; As well as in the synthesis of RNA. Pyridine is one of the important substances in the industrial chemistry as it is used in many of them, such as the pharmaceutical industry[(9-17)], the manufacture of pesticides, the manufacture of rubber and adhesives., It is also used in the organic synthesis as a solution (solvent) and as a reaction. The global production of this substance in 1989 reached about 26 thousand tons. Then it has increased steadily since the early 2000s, with annual production capacity reaching 30,000 tons in China alone. Pyridine is used in the preparation of pesticides mainly as a precursor to the production of herbicides, Pyridine is widely used as a ligand in harmonic complex chemistry[(18-24)], as well as with dipyridine (piperidine) and triperidine (terpyridine)[(25-33)]. When the pyridine ligament is part of the orthogonal complex, it is easy to replace it with a strong Lewis base[(34-37)]. This property is used in catalyzing the polymerization process, and in hydrogenation reactions using, for example[(38-42)], a Crabtree catalyst

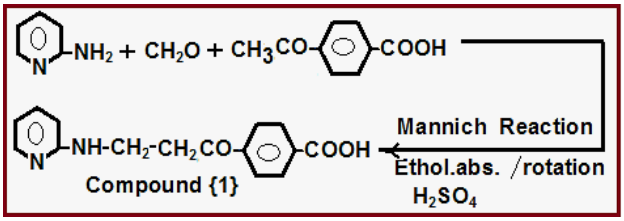
2. EXPERIMENTAL PART

Numerous indicative techniques have been applied to identify the synthesized compounds like ((FT-IR spectra (FT-IR 8300 Shimadzu) in the range (400-4000) cm^{-1} with KBr-discs., ^{1}H.NMR–Spectra in (DMSO)–solvent., Mass -Spectra .,besides to antimicrobial studies.

Preparation Processes[6-10]:

Synthesis Path of Compound{1}

Compound {1} prepared via mannich reaction through 2-amino pyridine (0.01 mole) reacted with p-acetobenzoic acid (0.01 mole) with formalin in presence of sulfuric acid with mechanical rotation for (4 hrs)in absolute ethanol according to methods[6-10] to produce precipitation that represented by Compound{1}, after that, filtered, dried, then re-crystallized to yield compound {1}.



Scheme 1 Synthesis of Compound{1}

Synthesis Path of Compound{2}

Compound {1} (0.01 mole) reacted with thiosemicarbazide (0.01 mole) in presence of absolute ethanol as a solvent and (H_2SO_4) in refluxing and rotation for (22 hrs) according to methods[6-10] to produce precipitation that represented by Compound{2}.

Synthesis Path of Compound{3}

Compound {1} (0.01 mole) reacted with thiosemicarbazide (0.01 mole) in presence of absolute ethanol as a solvent and (NaOH) in refluxing and rotation for (24 hrs) according to methods[6-10] to produce precipitation that represented by Compound{3}.

Synthesis Path of Compound{4}

Compound {1} (0.01 mole) reacted with semicarbazide (0.01 mole) in presence of absolute ethanol as a solvent and (H_2SO_4) in refluxing and rotation for (19 hrs) according to methods[6-10] to produce precipitation that represented by Compound{4}.

Synthesis Path of Compound{5}

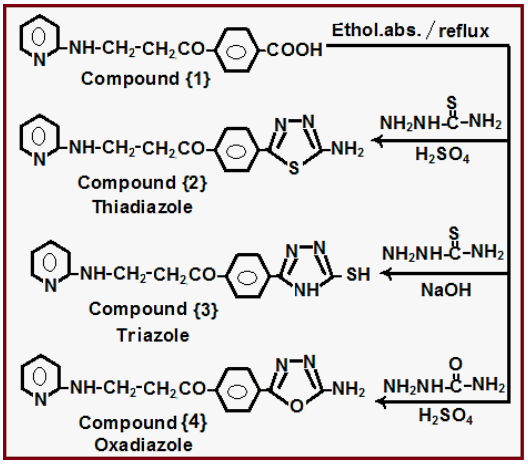
Compound {1} (0.01 mole) reacted with phenylene diamine (0.01 mole) in presence of (4N of HCl) in refluxing and rotation for (9 hrs) according to methods[6-10] to produce precipitation that represented by Compound{5}.

Synthesis Path of Compound{6}

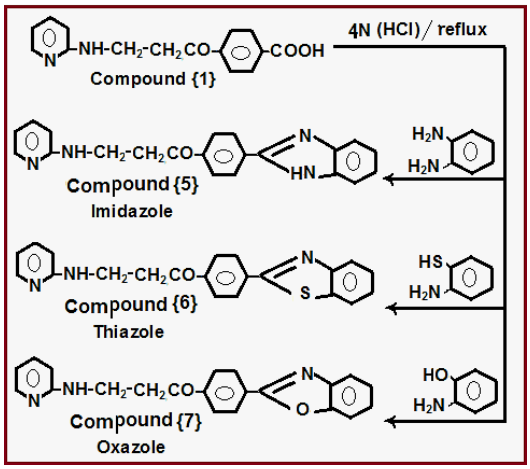
Compound {1} (0.01 mole) reacted with o-thiol aniline (0.01 mole) in presence of (4N of HCl) in refluxing and rotation for (9 hrs) according to methods[6-10] to produce precipitation that represented by Compound{6}.

Synthesis Path of Compound{7}

Compound {1} (0.01 mole) reacted with o-amino phenol (0.01 mole) in presence of (4N of HCl) in refluxing and rotation for (9 hrs) according to methods[6-10] to produce precipitation that represented by Compound{7}.



Scheme 2 Synthesis of Compounds{2,3,4}



Scheme 3 Synthesis of Compounds{5,6,7}

3. RESULTS AND DISCUSSION

The prepared heterocyclic compounds of pyridine have been studied by various chemical techniques and microbial studies:

Spectral Evidences of Prepared Compounds

FT.IR- Identification of Synthesized Compounds: The bands of functional groups in spectra gave strong evidences for new synthesized compound via disappearance of bands and appearance other new bands that indicate to preparation of the new compounds that represented by:

Compound **{1}:** appearance band at (3247)Cm^{-1} due to (NH) of amine group, band at (1700) due to carbonyl of ketone (-CO-), band at (2951) due to (CH) aliphatic, band at (1730) due to carbonyl of carboxyl group (-CO-O), band at (2635- 3155) due to (OH) of carboxyl group.

Compound **{2}:** appearance band at (3200)Cm^{-1} due to (NH) of amine group ,band at (1720) due to carbonyl of ketone (-CO-), band at (2900) due to (CH) aliphatic, bands at (3320, 3340) due to (NH_2) amine group, band at (1645) due to (C=N) endocycle of thiadiazole, band at (817) due to (C-S).

Compound **{3}:** appearance band at (3245)Cm^{-1} due to (NH) of amine group, band at (1711) due to carbonyl of ketone (-CO-), band at (2933) due to (CH) aliphatic, bands at (2410) due to (SH)thiol group, band at (1639) due to (C=N) endocycle of triazole.

Compound **{4}:** appearance band at (3198)Cm^{-1} due to (NH) of amine group, band at (1714) due to carbonyl of ketone (-CO-), band at (2983) due to (CH) aliphatic, bands at (3349, 3312) due to (NH_2) amine group, band at (1650) due to (C=N) endocycle of oxadiazole, band at (1191) due to (C-O-C) in oxadiazole.

Compound **{5}:** appearance band at (3218)Cm^{-1} due to (NH) of amine group, band at (1704) due to carbonyl of ketone (-CO-), band at (2961) due to (CH) aliphatic, band at (1647) due to (C=N) endocycle of imidazole.

Compound **{6}:** appearance band at (3201)Cm^{-1} due to (NH) of amine group ,band at (1700) due to carbonyl of ketone (-CO-), band at (2935) due to (CH) aliphatic, band at (1642) due to (C=N) endocycle of thiazole.

Compound **{7}:** appearance band at (3238)Cm^{-1} due to (NH) of amine group ,band at (1709) due to carbonyl of ketone (-CO-), band at (2922) due to (CH) aliphatic, band at (1656) due to (C=N) endocycle of oxazole.., Other frequencies appeared in some figures (1, 2).

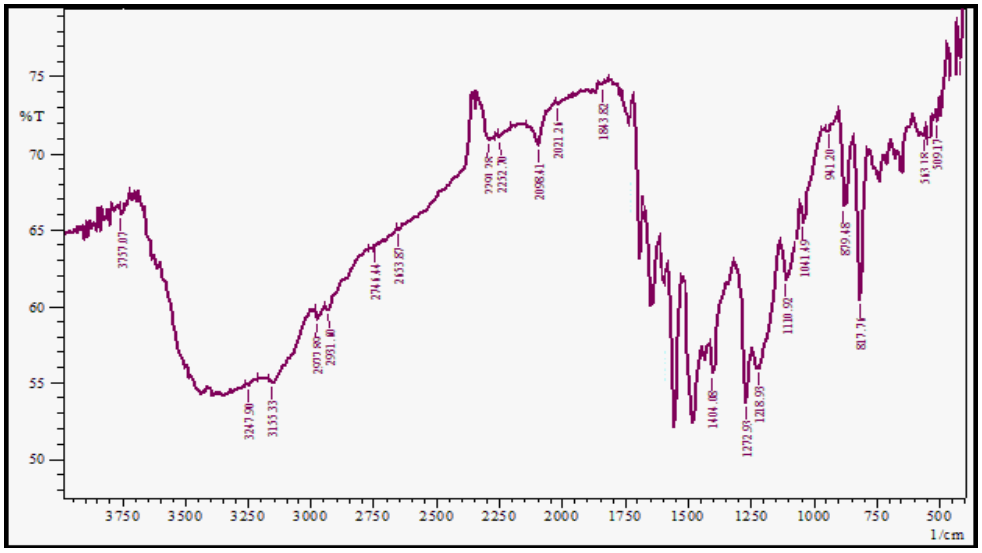


Fig. 1 I.R Spectrum of the Prepared Compound {1}

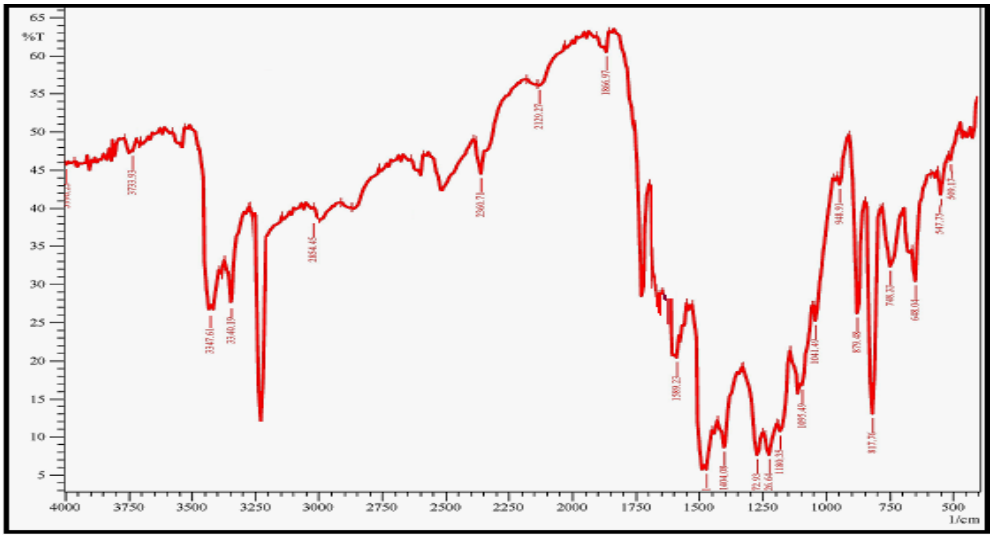


Fig. 2 I.R -Spectrum of the Prepared Compound {2}

[1]H.NMR-Characterization of New Compounds: The signals of functional groups in spectra also gave strong evidences for new synthesized compound via disappearance of peaks and appearance other new peaks that indicate to preparation of the new compounds that represented by:

Compound {1}: signal at (5.01) due to proton of amine group (NH), signals at (1. 82, 1. 86, 1. 97) due to protons of (-CH_2-CH_2-CO), signals at (6. 79-7. 64) due to protons of phenyl ring, signal at (12.05) due to proton of carboxyl group (COOH).

Compound {2}: signal at (4.86) due to proton of amine group (NH), signals at (1. 32, 1. 34, 1. 37) due to protons of (-CH_2-CH_2-CO), signals at (7. 41-7. 85) due to protons of phenyl ring, signal at (4.92) due to proton of amine group (NH_2).

Compound {3}: signal at (4.37) due to proton of amine group (NH), signals at (1. 34, 1. 35, 1. 37) due to protons of (-CH_2-CH_2-CO), signals at (7. 41-7. 88) due to protons of phenyl ring, signal at (5.36) due to proton of thiol group (-SH).

Compound {4}: signal at (4.90) due to proton of amine group (NH), signals at (1. 30, 1. 38, 1. 44) due to protons of (-CH_2-CH_2-CO), signals at (7. 12-7. 89) due to protons of phenyl ring, signal at (4.97) due to proton of amine group (NH_2).

Compound {5}: signal at (4.93) due to proton of amine group (NH), signals at (1. 29, 1. 30, 1. 39) due to protons of (-CH_2-CH_2-CO), signals at (7. 32 -7. 88) due to protons of phenyl ring.

Compound {6}: signal at (4.86) due to proton of amine group (NH), signals at (1. 21, 1. 22, 1. 28) due to protons of (-CH_2-CH_2-CO), signals at (7. 00 -7. 81) due to protons of phenyl ring.

Compound {7}: signal at (4.99) due to proton of amine group (NH), signals at (1. 20, 1. 31, 1. 36) due to protons of (-CH_2-CH_2-CO), signals at (7. 18 -7. 85) due to protons of phenyl ring.

Some peaks in some figures (3, 4).

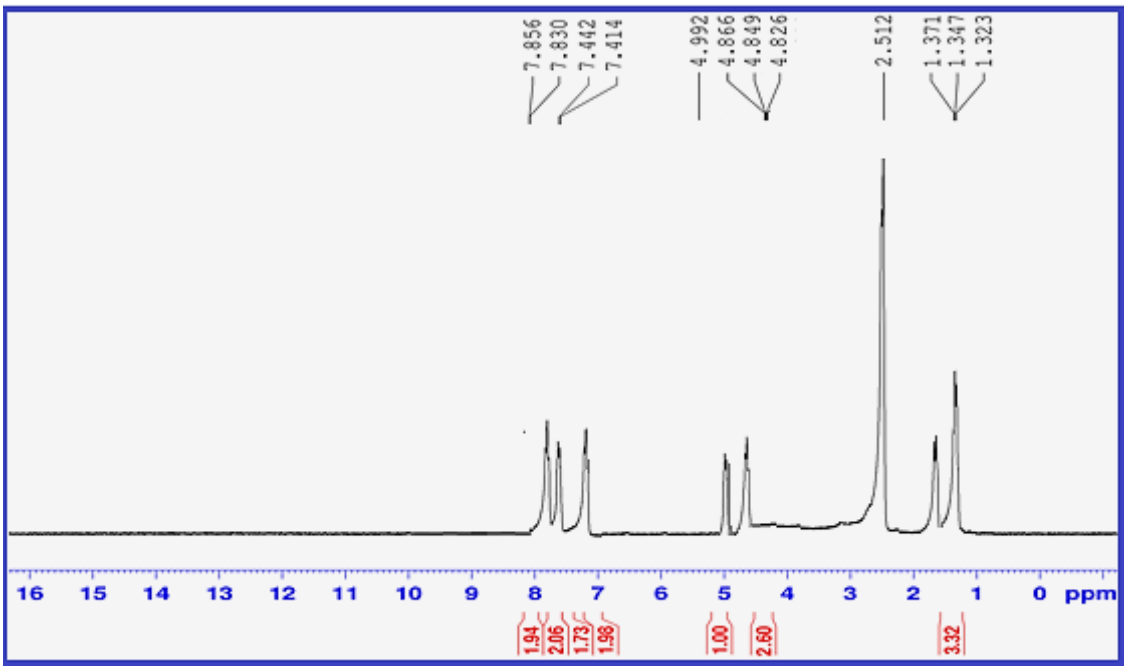


Fig. 3 H.NMR-Spectrum of Compound{2}

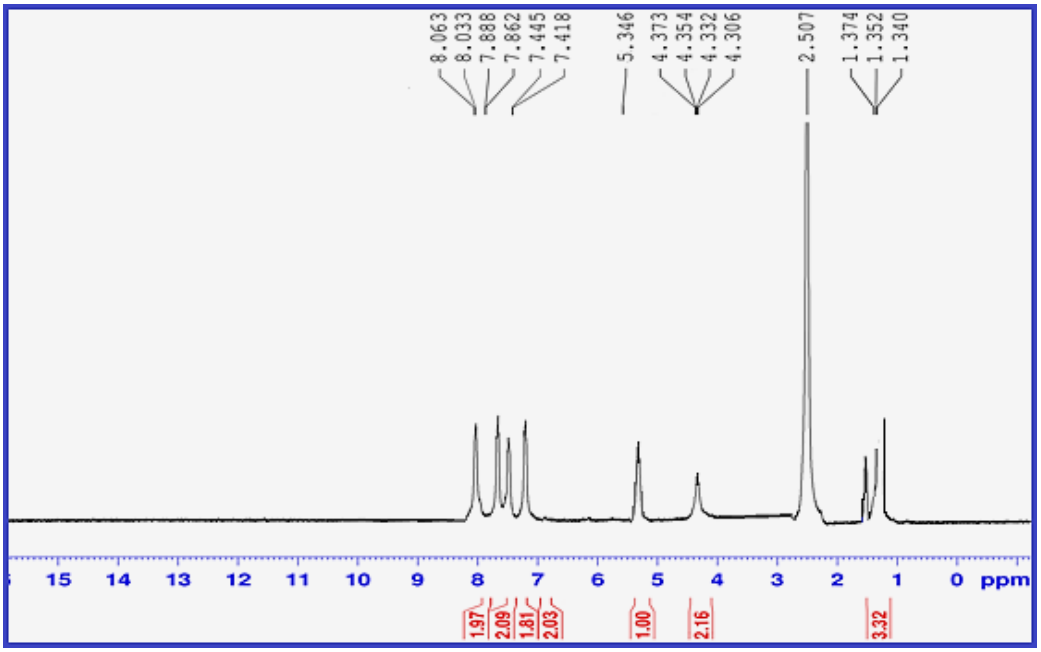


Fig. 4 H.NMR-Spectrum of Compound{3}

Mass –Spectra of New Compounds: Some of the new pyridyl-cyclic compounds have been screened in mass spectra, it was found same formatted structures of prepared compounds via compared with fragments of compounds in spectra., Some of spectra are appeared in figures (5 ,6).

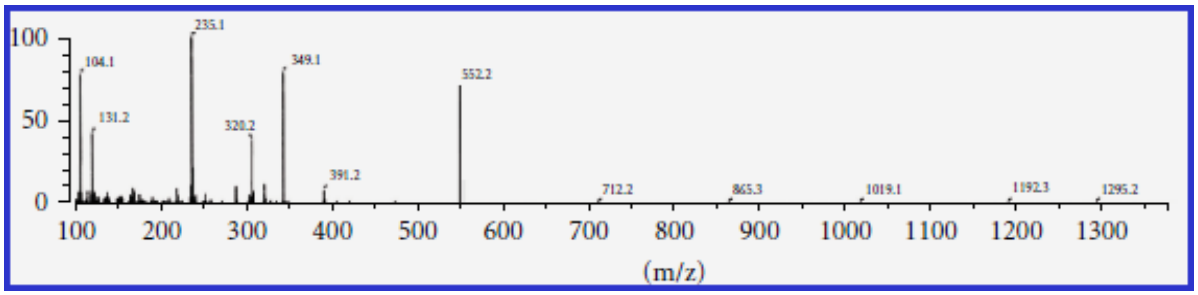


Fig. 5 Mass–Spectrum of Compound{2}

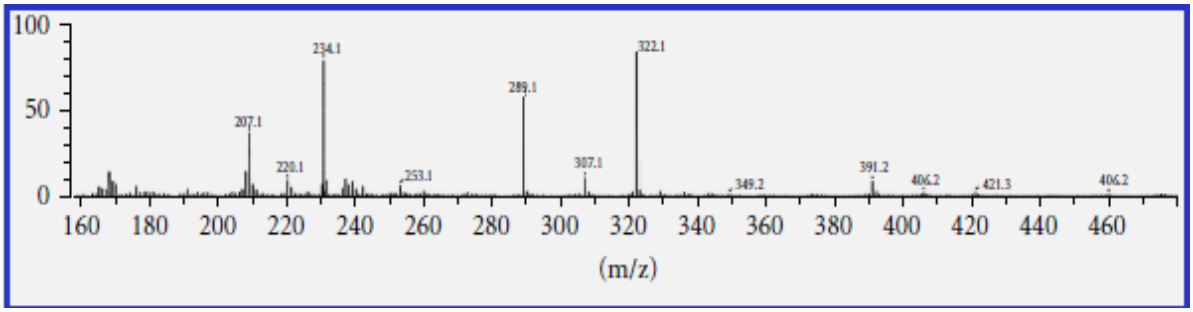


Fig. 6 Mass-Spectrum of Compound{3}

Some Physical and Chemical Properties and Measurements

All other physical and chemical analysis and some characterization in Table (1):

Table 1: Some Physical Properties of New Compounds

Comps	*Product %*	*Color*	*M .P (C °)*	*Rf*	*Solvents (TLC)*
{1}	80	Yellow	148	0.60	Ethanol : Benzene
{2}	82	Yellowish orange	192	0.62	Ethanol : Benzene
{3}	76	Orang	198	0.58	Ethanol : Benzene
{4}	70	Reddish Yellow	204	0.60	Ethanol : Benzene
{5}	70	Orange	218	0.62	Ethanol : Benzene
{6}	72	Yellowish Red	210	0.66	Ethanol : Benzene
{7}	74	Yellowish Orang	230	0.60	Ethanol : Benzene

Antimicrobial Assay[30, 40]:

All pyridyl-cyclic compounds screened for their antibacterial assay via agar through the flowing several procedure[40]. The investigation of microbial inhibition performed at (three concs) (20, 30, 50 micro gram) concentrations in best solvent (DMSO) with bacteria: ***(Proteus mirabilis, St. aureus)***. The selected types of bacteria incubated for (24 hr) at (37ºC). The assay of pyridyl–cyclic compounds against types of bacteria gave good results with compounds {2 and 3} more than other compounds due to (sulfur and nitrogen) -atoms in same compounds that participates in inhibition of bacteria., all results in Table (2) and photo (1):

Table 2: Inhibition test of compounds in Conc. (30 micro gram)

Compounds	*P. mirabilis*	*St. aureus*
Compound {1}	+	+
Compound {2}	+++	+++
Compound {3}	+++	+++
Compound {4}	++	++
Compound {5}	++	++
Compound {6}	++	++
Compound {7}	++	++

(+): inhibition (4-8) mm
(++): inhibition (9-12) mm
(+++): inhibition (13-18) mm

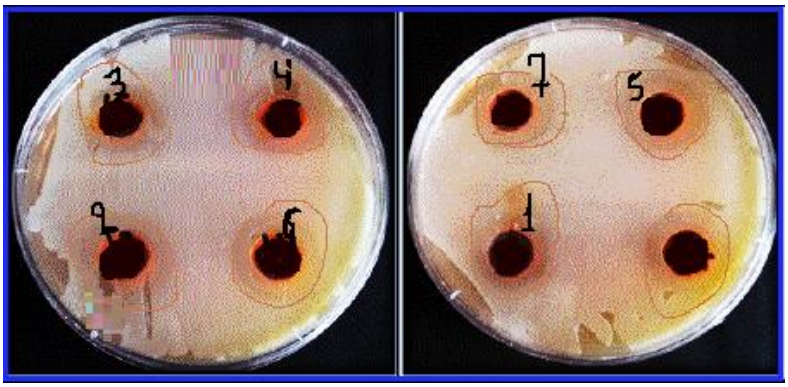


Photo 1 Inhibition of Compounds on St. aureus

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Ethical clearance: Ethics committee refer that there is no plagiarism and there is no mistakes or wrong results in this work.

Conflict of interest: The authors declare that there is no conflict of interest.

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