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SYNTHESIS OF 1-OXO-1, 2, 3, 4, 9, 10-HEXAHYDROXANTHENE DERIVATIVES CATALYZED BY ZN-MONTMORILLONITE AND THEIR EVALUATION OF BIOLOGICAL ACTIVITY

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ABSTRACT
A novel approach for the synthesis of 1-Oxo-1, 2, 3, 4, 9,10-hexahydroxanthene derivatives (**IIIa-j**) from 1,3-cyclohexane dione or dimedone and substituted salicylaldehydes is described using a catalytic amount of Zinc montmorillonite as catalyst at heating conditions in the presence of ethanol and catalytic amount of DMF media. The results presented that the reaction executed under these conditions were good to the environment, simple operation, convenient separation, inexpensive, with higher yields and easy workup procedure. The catalyst was quantitatively recovered from reaction mixture by simple filtration and reused for three cycles with consistence activity.
All these compounds have been characterized by modern spectral techniques such as IR, ^{1}H NMR, Mass etc. Evaluation of synthesized compounds for antimicrobial activity against specific bacterial strains like 1) *Bacillus pumilis* 2) *Bacillus subtilis* 3) *Echerichia coli* 4) *Protius vulgari*, along with antifungal activity against 1) *Aspergillus niger*, 2) *Rhizopus oryzae* and 3) *Aspergillus flavus*.

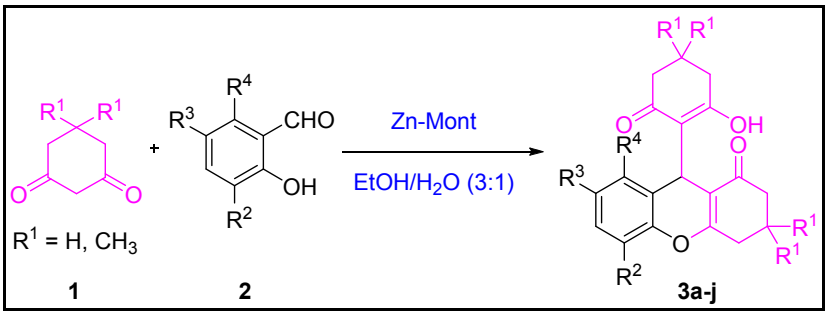
KEYWORDS: Zn-montmorillonite, Green chemistry, Salicylaldehyde, 1, 3-Cyclohexane dione, Hexahydroxanthene, Antimicrobial activity.

INTRODUCTION

In the past few decades, the synthesis of new heterocyclic compounds has been a topic of great attention due to their extensive applicability. Xanthenes and its derivatives are important in the area of medicinal chemistry. Xanthene derivatives are very important class of heterocyclic compounds have been extensively used as dyes [I], fluorescent materials for imagining of biomolecules and in laser technologies [II]. Xanthenes have wide range of biological and therapeutic properties such as antibacterial, antiviral and anti-inflammatory actions as good as in photodynamic therapy [III, IV]. They have also been reported for their agricultural bactericide activity [V], anti-inflammatory [VI] and antiviral activity [VII]. Due to their extensive range of applications, these compounds have usually a great deal of attention in linking with their synthesis. A wide change of methods for the preparation of the xanthenes have been reported in the recent years [VIII-XII].
The chemical and pharmaceutical industries are always under pressure to progress more environmentally friendly organic reaction methodologies. The progress of environmentally benevolent methods for the synthesis of heterocyclic compounds is one of the required goals in current organic chemistry to study added green procedures for the generation of the target molecules. In this regard, the increasing demand for cleaner procedures supported by stringent environmental laws necessitates use of eco-friendly and discriminating catalysts. Montmorillonite has been found to be suitable for heavy metals adsorption over cation exchange mechanism in the interlayer and the

formation of inner sphere complexes through Si–O and Al–O groups at the clay particle edges [XIII-XV]. These interlayer cations can undergo interchange with cations from external solutions. This property of K-10 has been activated to prepare zinc ion exchanged catalysts with various concentration of zinc. The catalytic activity of Zn/K-10 with optimum zinc filling has been compared with Zn/H-beta and Zn/silica. Research and industrial concentration has focused on the use of acid activated montmorillonite K10-supported zinc chloride (zinc montmorillonite, Zn^{2+}-mont); use of this significant material has been first reported in 1989 [XVI]. Illustrations for Zn^{2+}-montmorillonite-mediated organic reactions such as Intermolecular hydroamination of alkynes [XVII], synthesis of 1,1-diacetates from aldehydes, hydroamination, 3-Aza-Cope rearrangement etc. are reported earlier in the literature [XVIII-XXII]. Therefore, the search continues for a better catalyst for the synthesis of 1-Oxo--hexahydroxanthene in terms of reusability, operative easiness, economic feasibility.

Among the various synthetic procedures of 1-Oxo-hexahydroxanthene derivatives with earlier reported by other catalysts like, cellulose sulfuric acid [XXIII] and triethylbenzylammoium chloride [TEBA] [XXIV]. In our previous study, we reported the $CeCl_3 \cdot 7H_2O$ catalyzed synthesis of 1-Oxo-1, 2, 3, 4, 9, 10-hexahydroxanthene derivatives using salicylaldehydes and dimedone [XXV]. In continuation of our interest in developing novel synthetic methodologies, particularly carbon-carbon, carbon-heteratom bond formations, and in the use of Zn^{2+}-montmorillonites as environmentally friendly reagents for organic synthesis, we undertook a study of the utility of Zn^{2+}-mont as catalyst for the synthesis of 1-oxo-1,2, 3,4,9,10-hexahydroxanthene derivatives (**Scheme 1**).



Scheme 1: Synthesis of 1-Oxo-1, 2, 3, 4, 9, 10-hexahydroxanthene derivatives using Zn-montmorillonite.

All the synthesized compounds have tested in vitro for their antibacterial (*Bacillus pumilis, Bacillus Subtilis, Echerichia coli,Protius vulgaris*) and antifungal (*Aspergillus niger, Rhizopus oryzae, Aspergillus flavus*) activities. Compounds **IIIc**, **IIIf**, and **IIIh**, were showed most potent in vitro activity against bacterial and fungal strains. However, to the best of our knowledge, there are no earlier reports on the preparation of 1-Oxo-1,2, 3,4,9,10-hexahydroxanthene derivatives using Zn^{2+}-mont todate.

RESULTS AND DISCUSSION

CHEMISTRY:

We have tested the practicability of the reaction of 2 eq of 1,3-cyclohexane dione (**I**, 2 mmol) and 1 eq of salicilaldehyde (**IIa**, 1 mmol) using various Zn^{2+}-mont at heating conditions in the presence of ethanol and catalytic amount of DMF media. to afford the corresponding 1-Oxo-1, 2, 3, 4, 9, 10-hexahydroxanthene derivatives **IIIa-j** with 86-96% yield. Correspondingly, various substituted salicylaldehydes reacted smoothly with cyclohexanedione, resultant in good yields of products. Dimedone also reacted well with substituted salicylaldehydes, giving the resultant products in high yields, and the results are indicated in **Table 1**. The crude products are purified by recrystallization from 95% EtOH. All the products are characterized by IR, ^{1}H NMR, and mass spectral analysis and also by comparison with authentic samples. Since a number of 1-Oxohexahydroxanthenes reported to possess biological activities like antibacterial and anti-fungal activities; it is thought worthwhile to screen them for these activities (Table 1).

Table 1: Zn-montmorinilite heterogenous catalyst-catalyzed synthesis of 1-Oxo-hexehydroxanthenes[a,b] in ethanol:water (3:1; v/v) media.

Entry	R^1	R^2	R^3	R^4	Time (h)	Yield (%)	MP (°C)
IIIa	H	H	H	H	3	83	226
IIIb	H	H	Cl	H	4	84	220
IIIc	H	OCH_3	H	H	3	89	232
IIId	H	Br	$C(CH_3)_3$	H	3	90	201
IIIe	H	$C(CH_3)_3$	$C(CH_3)_3$	H	3	87	211
IIIf	CH_3	H	H	H	4	91	204
IIIg	CH_3	H	Cl	H	3	94	228
IIIh	CH_3	OCH_3	H	H	4	91	222
IIIi	CH_3	Br	$C(CH_3)_3$	H	4	83	212
IIIj	CH_3	$C(CH_3)_3$	$C(CH_3)_3$	H	4	81	216

[a]All products were characterized by spectral data and compared with authentic samples.
[b]Isolated pure products.

ANTIBACTERIAL ACTIVITY:

"All the synthesized 1-Oxo-hexehydroxanthenes derivatives (**Table 2, Figure 1**), **IIIa-j** were screened for their antibacterial activity against different types of bacterial strains" [XXVI], they are "Gram positive bacterial strains of *Bacillus pumilis and Bacillus subtillis*, Gram negative bacterial strains of *Escherichia coli and Protius vulgaris"* [XXVII], at a concentration of 100 µg/mL. Some of the synthesized compounds showed high activity and some showed moderate activity compared to standard drug *Ampicillin* at a concentration of 100 µg/mL. The antibacterial activity of compound **IIIc** (R^2 = -OCH_3), **IIIf** (R^1 = -CH_3) and **IIIh** (R^1 = -CH_3, R^2 = -OCH_3) showed good zone of inhibition against *Bacillus pumilis*, *Bacillus Subtilis*, *Echerichia coli*, and *Protius vulgaris* compared to the standard drug at a concentration of 100 µg/ mL. Whereas the compounds **IIIa, IIId, IIIi** and **IIIj** were showing moderate activity against all the bacterial strains when compared to standard drug *Ampicillin* at a concentration of 100 µg/ mL. Compounds **IIIb**, **IIIe** and **IIIg** weren't showing activity against *P. vulgaris* bacteria. It leads us to conclude that from **Table 2** and **Figure 1**, methoxy and methyl substituted compounds showed higher zone of inhibition when compared with other compounds. Furthermore, substitutions like -$C(CH_3)_3$, Cl and Br, did not provide any significant change in the levels of activity against bacterial strains (Table 2, Figure 1).

Table 2: Antibacterial activity of 1-oxohexahydroxanthenes (3a-j)

Compound	R^1	R^2	R^3	R^4	Zone of inhibition in (mm)			
					B. pumilis	*B. subtilis*	*E. coli*	*P. vulgaris*
IIIa	H	H	H	H	6	7	8	4
IIIb	H	H	Cl	H	3	5	6	-

IIIc	H	OCH_3	H	H	9	10	11	7
IIId	H	Br	$C(CH_3)_3$	H	2	6	7	1
IIIe	H	$C(CH_3)_3$	$C(CH_3)_3$	H	2	4	4	-
IIIf	CH_3	H	H	H	6	7	9	4
IIIg	CH_3	H	Cl	H	5	6	6	-
IIIh	CH_3	OCH_3	H	H	8	10	10	7
IIIi	CH_3	Br	$C(CH_3)_3$	H	3	5	6	3
IIIj	CH_3	$C(CH_3)_3$	$C(CH_3)_3$	H	4	6	7	2
Ampicillin (10 µg/mL					20	24	19	18

Concentration of the test compound: 100 µg/ mL.

Figure 1

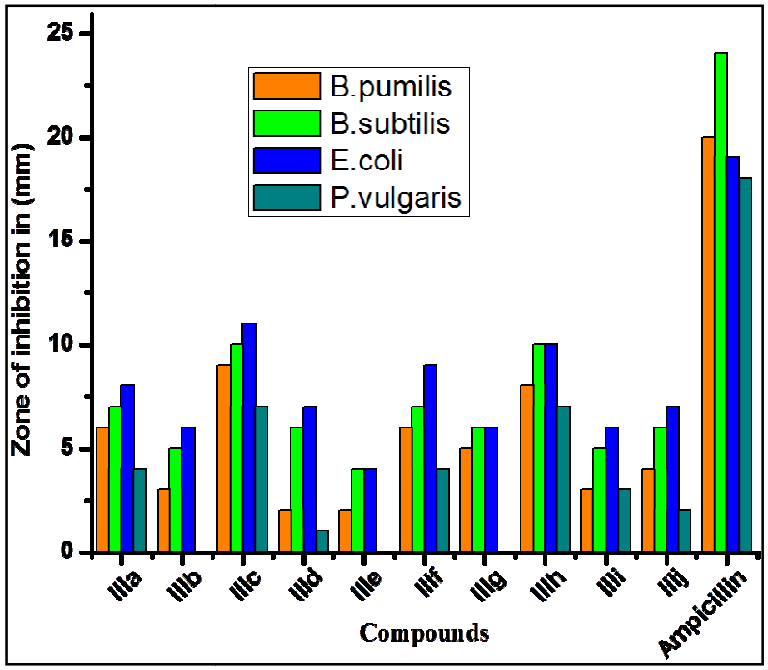


Figure 1: Antibacterial activity of compounds **IIIa-j** against *Bacillus pumilis*, *Bacillus Subtilis*, *Echerichia coli* and *Protius vulgaris*. Micro organism were screened using potato dextrose agar with *Bacillus pumilis*, *Bacillus subtilis*, *Echerichia coli* and *Protius vulgaris* are showing zone of inhibition (mm) with different concentration of compound.

ANTIFUNGAL ACTIVITY:

The antifungal activity of 1-Oxohexahydroxanthene derivatives have been evaluated against *A. niger*, *R. oryzae* and *A. flavus* by employing Clotrimazole (10 mg) as the standard drug. 5-Bromo-tert-butyl- 3, 5-ditert-butyl, 5-chloro substituted 1-oxohexahydroxanthene derivative showed mild antifungal activity against *A. niger* and *R. oryzae*. Compounds **IIIb**, **IIIe**, **IIIh**, **IIIi** and **IIIj** did not showed activity against *A. flavus*. Compounds**IIIa**, **IIIc** and **IIIf** showed activity against *A. niger*, *R. oryzae*, *A. flavus*. The antifungal activity of synthesized 1-Oxo-hexahydroxanthenes derivatives (**Table 3, Figure 2**) **IIIa-j** were tested against three pathogenic fungi, namely *Aspergillus niger, Rhizopus oryzae* and *Aspergilus flavus*, by the cup plate at a concentration of 100 µg/mL [XXVIII]. Some of the synthesized compounds showed moderate to good antifungal activity compared to standard drug Clotrimazole at a concentration of 100 µg/mL. The antifungal activity of compounds **IIIa, IIIc** (R^2 = -OCH_3) and **IIIf** (R^1 = -CH_3) showed good zone of inhibition against *Aspergillus niger, Rhizopus oryzae* and *Aspergilus flavus* compared to the standard drug. Compound **IIIh** (R^1 = -CH_3, R^2 = -OCH_3) was showing good antifungal activity against *Aspergillus niger* and *Rhizopus oryzae*, except *Aspergilus flavus.*The electron

donating groups such as metoxy and methyl substituted groups showed better antifungal activity and which could seen in the case of IIIc, IIIf and IIIh. However the substitution by halogens or $–C(CH_3)_3$, did not provide any significant change in the levels of activity against fungi (Table 3, Figure 2).

Table 3: Antifungal activity of 1-oxohexahydroxanthenes (IIIa-j)

Compound	R^1	R^2	R^3	R^4	Zone of inhibition in (mm)		
					A. niger	*R. oryzae*	*A. flavus*
IIIa	H	H	H	H	5	7	2
IIIb	H	H	Cl	H	2	1	-
IIIc	H	OCH_3	H	H	7	6	3
IIId	H	Br	$C(CH_3)_3$	H	2	4	1
IIIe	H	$C(CH_3)_3$	$C(CH_3)_3$	H	3	3	-
IIIf	CH_3	H	H	H	5	7	3
IIIg	CH_3	H	Cl	H	4	3	1
IIIh	CH_3	OCH_3	H	H	6	8	-
IIIi	CH_3	Br	$C(CH_3)_3$	H	3	3	-
IIIj	CH_3	$C(CH_3)_3$	$C(CH_3)_3$	H	3	2	-
Clotrimazole (10 µg/mL					20	18	16

Concentration of the test compound: 100 µg/mL.

Figure 2

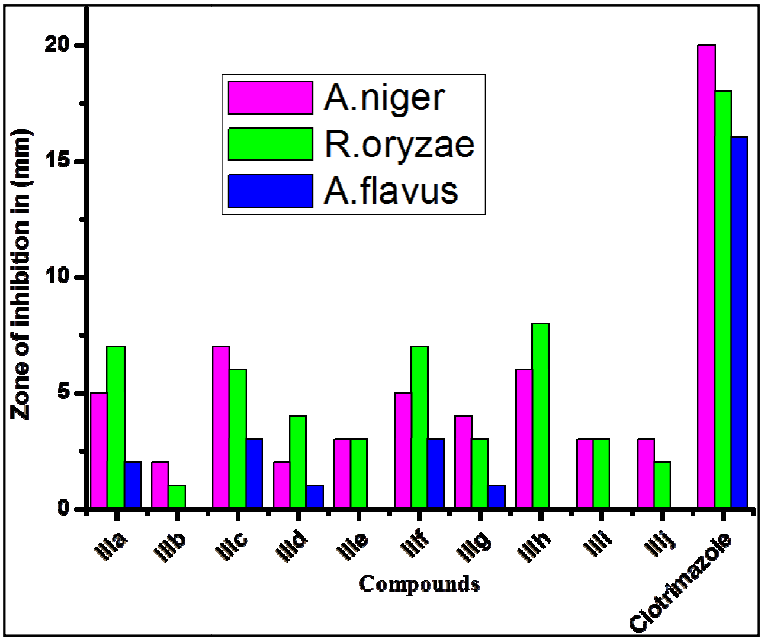


Figure 2: Anti fungal activity of compounds **IIIa-j** against *Aspergillus niger, Rhizopus oryzae* and *Aspergillus flavus*. Micro organism were screened using potato dextrose agar with *Aspergillus niger, Rhizopus oryzae* and *Aspergillus flavus* are showing zone of inhibition (mm) with different concentration of compound.

CONCLUSION

In conclusion, we have developed a new and efficient method for the synthesis of 1-oxo-hexahydroxanthene in excellent yields using zinc montmorillonite as catalyst at room temperature in the presence of ethanol and catalytic amount of DMF media. Compared to other methods, this new method has the lead of good yields, inexpensive reagents, easily available, easy workup, mild reaction conditions, environmentally friendly reaction conditions, reusable catalyst makes this method simple,

clean, practical, and economically viable. We believe this methodology is superior to remaining methodologies for the synthesis of 1-oxo-hexahydroxanthene. The *in vitro* antibacterial, antifungal evaluation showed that most of the synthesized 1-oxo-hexahydroxanthenes derivatives exhibited moderate to good zone of inhibition. From the results of antibacterial and antifungal activity of 1-oxo-hexahydroxanthenes it is interesting to note that substituents like methoxy and methyl, substituents shows better antibacterial and antifungal activity compared to other substituted compounds. Noticeably, compound **IIIc**, **IIIf**, **IIIh**, were most potent compound *in vitro* activity against bacterial and fungal strains. These findings demonstrated that 1-oxo-hexahydroxanthenes have biological significance; further optimization of this series as well as preparation of new, 1-oxo-hexahydroxanthenes derivatives are ongoing in our laboratory.

EXPERIMENTAL SECTION:

All reactions were monitored by thin-layer chromatography (TLC) using silica-coated plates and visualization under UV light. Light petroleum of the distillation range 60–80°C was used. Melting points were determined using a Buchi R-535 apparatus and are uncorrected. Mass spectra were recorded under electron impact at 70 eV on an LC-MSD (Agilent Technologies). ^{1}H NMR spectra were recorded on Varian FT 200-MHz (Gemini) and Bruker UXNMR FT 300-MHz (Avance) instruments in $CDCl_3$. Chemical shift values were reported in parts per million (d) relative to tetramethylsilane (TMS) (δ 0.0) as an internal standard. EtOH 95% was used for recrystallization. Yields refer to pure products isolated by crystallization and spectroscopically (^{1}H, IR) homogeneous material.

GENERAL PROCEDURE FOR THE SYNTHESIS OF COMPOUNDS IIIa-j:

A mixture of 1 equiv. of substituted salicylaldehyde **II** (1.0 mmol) and 2 equiv. of cyclohexane1,3-dione or dimedone **I** (1.0 mmol) in the presence of Zn-Montmorinilite (50 mg) heterogenous catalyst in ethanol and catalytic amount of DMF was stirred at 60 °C for 1.5–5 h. The completion of the reaction was monitored by TLC. After completion of reaction, the catalyst was separated by simple filtration, washed with Ethanol and reused for several cycles. The crude product was washed with water and purified by recrystallization from 95% EtOH to give 1-Oxo-1, 2, 3, 4, 9, 10-hexahydroxanthene derivatives (**IIIa-j**) in high yields (see **Table 1**). The structure of the products was confirmed by spectral data (^{1}H NMR, IR, mass).

Spectral Data [XXV]

Compound IIIa

Mp 226 °C; IR (KBr): 3150, 2920, 2880, 1640, 1570, 1550, 1485, 1440, 1360, 1280, 1220, 1180, 1051, 991, 970, 905, 840 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 1.92-2.75 (m, 12H, $6CH_2$), 4.60 (s, 1H, CH), 7.98-7.05 (m, 3H, ArH), 7.01-7.20 (m, 1H, ArH), 10.81 (s, 1H, OH); ESI MS: m/z 310 [M$^+$].

1. Antibacterial activity by cup plate method:

The antibacterial activity of synthesized compounds was conducted against two gram positive bacteria viz., *Bacillus subtilis, Bacillus pumilis*, and two gram negative bacteria viz., *Escherichia coli* and *Proteus vulgaris* by using cup plate method. Ampicillin sodium was employed as standard to compare the results.

Culture medium: Nutrient broth was used for the preparation of inoculum of the bacteria and nutrient agar was used for the screening method.

Composition of nutrient agar medium:

Peptone	–	5.0 gm
Sodium chloride	–	5.0 gm
Beef extract	–	1.5 g
Yeast extract	–	1.5 g
Agar	–	15.0 g
Distilled water upto	–	100 mL
pH	–	7.4 $\pm$ 0.2

The test organisms were subcultured using nutrient agar medium. The tubes containing sterilized medium were inoculated with respective bacterial strain. After incubation at 37°C $\pm$ 1°C for 24 h, they were stored in refrigerator. Bacteria inoculum was prepared by transferring a loopful of stock culture

to the nutrient broth (100 mL) in conical flasks (250 mL). The flasks were incubated at 37°C ± 1°C for 48 h before the experimentation.

Solutions of the test compounds were prepared by dissolving 10 mg each in dimethylformamide (10 ml Anal R. grade). A reference standard for both gram positive and gram negative bacteria was made by dissolving accurately weighed quantity of Ampicillin sodium in sterile distilled water, separately.

The nutrient agar medium was sterilized by autoclaving at 121°C (151 lb/sq.inch) for 15 min. The petriplates, tubes and flasks plugged with cotton were sterilized in hot-air oven at 160°C for an hour into each sterilized petriplate (10 cm diameter), about 27 mL of molten nutrient agar medium was poured and inoculated with the respective strain of bacteria (6 mL of inoculum to 300 mL of nutrient agar medium) aseptically. The plates were left at room temperature to allow the solidification. In each plate, three cups of 6 mm diameter were made with sterile borer. Then 0.1 mL of the test solution was added to the respective cups asceptically and labeled, accordingly. The plates were kept undisturbed for atleast 2 h in refrigerator to allow diffusion of the solution properly into nutrient agar medium. After incubation of the plates at 37°C ± 1°C for 24 h, the diameter of zone of inhibition surrounding each of the cups was measured with the help of an antibiotic zone reader. All the experiments were carried out in triplicate. Simultaneously, controls were maintained employing 0.1 mL of dimethylformamide to observe the solvent effects. The results are presented in **Table 2**.

2. Antifungal activity :

All those compounds screened for antibacterial activity were also tested for their antifungal activity. The fungi employed for screening were *Aspergillus niger*, *Rhizopus oryzae* and *Aspergillus flavus*.

The test compounds were sub-cultured using potato-dextrose-agar medium. The tubes containing sterilized medium were inoculated with test fungi and after incubation at 25°C for 48 h, they were stored at 4°C in refrigerator.

The inoculum was prepared by taking a loopful of stock culture to about 100ml of nutrient broth, in 250 mL conical flasks. The flasks were incubated at 25°C for 24 h before use.

The solutions of test compounds were prepared by a similar procedure described under antibacterial activity. A reference standard (1 mg/mL conc) was prepared by dissolving 10 mg of clotrimazole in 10 mL of dimethylformamide (Anala R grade). Further, the dilution was made with dimethylformamide it self to obtain a solution of 100 µg/mL concentration.

The potato-dextrose-agar medium was sterilized by autoclaving at 121°C (15 lb/sq.inch) for 15 min. The petriplates, tubes and flasks with cotton plugs were sterilized in hot-air oven at 150°C, for an hour. In each sterilized petriplate, about 27 mL of molten potato-dextrose-agar medium inoculated with respective fungus (6 mL of inoculum in 300 mL of potato-dextrose-agar medium) was added, asceptically. After solidification of the medium at room temperature, three cups of 6 mm diameter were made in each plate with a sterile borer 0.1 mL (100 µg/cup) of test solution was transferred accurately to the cups aseptically and labeled accordingly. The reference standard, 0.1 ml (10 µg/disc) was also added to the discs in each plate. The plates were kept undisturbed at room temperature atleast for 2 h to allow the solution to diffuse properly into the potato-dextrose-agar medium. Then the plates were incubated at 25°C for 48 h. The diameter of the zone of inhibition was read with the help of an antibiotic zone reader. The experiments were performed in triplicate in order to minimize the errors. The results are presented in **Table 3**.

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