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COPPER (I) ASSISTED CATALYST DIMERISATION OF TERMINAL ALKYNES AND THEIR ANTIBACTERIAL STUDIES

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ABSTRACT
Terminal alkynes undergo oxidative-coupling smoothly in the presence of the Cu(I)Cl catalytic system. The reaction gives 1,3-diynes in excellent yields under mild conditions. Structures of the all synthesized compounds were established based on TLC, FT-IR, ^{1}H NMR, and MASS spectral data. All the synthesized compounds were examined for antibacterial activity.
KEYWORDS: Cu (I) catalyst, Dimerisation, Terminal alkynes, 1, 3-diyn-diols.

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INTRODUCTION

1,3-Diynes are very important compounds in terms of their chemistry and the solid state properties of their homopolymers[1] The synthesis of diynes, in addition to the traditional Glaser oxidative coupling of terminal acetylenes[2], They can be achieved by Pd(0)–Cu(I) catalyzed self-coupling of terminal alkynes in the presence of chloroacetone[3], Ethyl bromoacetate[4], Allyl bromide[5] and iodine[6], Diynes were also prepared under standard Sonogashira cross-coupling conditions in the absence of an obvious oxidant[7].

In the present study, a series of dimers were prepared in presence of Cu(I) catalytic system in pyridine and the synthesized compounds were evaluated for antibacterial activity against *E. coli* and *S. aureus.*

MATERIALS AND METHODS

Analytical grade solvents and commercially available reagents were used without further purification. Melting points were determined in open capillary tube and are uncorrected. The completion of the reaction and purity of the compounds were checked by thin layer chromatography (TLC). IR spectra in KBr disk were recorded from 4000 to 400 cm-1 on Avatar 330 FT-IR spectrometer equipped with DTGS detector. ^{1}H NMR spectra were recorded on GEOL-JMS D–300 (MHz) NMR using $CDCl_3$ as the solvent with trimethylsilane (TMS) as an internal standard. MASS spectra were recorded on Shimandzu GC-MS (at 70 eV) Mass Spectrometer using xenon as the carrier gas.

General procedure for synthesis of Dimer molecules (1-6)

Terminal alkyne (0.01 mole) was dissolved in 10 ml of methanol, and 0.5g of copper (I) chloride in 3 ml of dry pyridine were added. These contents are stirred under oxygen atmosphere for 2 hrs. Reaction completion was checked by using TLC in hexane and ethyl acetate mixture (70:30). After completion of the reaction mixture neutralized with Conc. HCl and 25 ml saturated sodium chloride were added. These reaction mixtures kept for the refrigerator for whole night and filter the precipitated product. The product washed with cooled water to remove the colour impurities and dried in the air. The product is recrystalized in methanol. (**Scheme 1**)

Antibacterial activity

The antibacterial activity was determined using disc diffusion method by measuring the zone of inhibition in mm. All the synthesized compounds were evaluated antibacterial activity against *Escherichia coli* (gram negative), *Staphylococcus aureus* (gram positive) bacterial strains. The compounds were tested at a concentration of 50 µg/mL. Ampicillin was used as a control[8]. The results are given in **Table 2**.

SPECTRAL DATA

Compound-1: Propargyl alcohol dimer: Molecular formula : $C_6H_6O_2$, Molecular weight : 110.11. **FTIR (KBr) in cm^{-1}:** 3283.42 (O-H Str), 2924.17 (C-H Str), C≡C (no absortion) **^{1}H NMR (500 MHz, DMSO) :** δ

3.32 (2H, S, CH_2), 2.508 (S, 1H of Hydroxyl). **MASS :** 111 (M^+)**.**

Compound-2: 1-Pentyne-3-ol dimer: Molecular formula : $C_{20}H_{18}O_2$, Molecular weight : 290.35. **FTIR (KBr) in cm^{-1}:** 3434.82 (O-H Str), 2921.42 (C-H Str), C≡C (no absortion). **^{1}H NMR (500 MHz, DMSO) :** 3.2-3.5 (2H, m, CH_2), 2.4-2.6 (1H, t), 2.3-2.4 (3H, t), 2.12 (S, 1H of Hydroxyl). **MASS :** 291 (M^+)**.**

Compound-3: 1-octyne-3-ol dimer: Molecular formula: $C_{16}H_{22}O_2$, Molecular weight: 246.34.

FTIR (KBr) in cm^{-1}: 3441.07 (O-H Str), 2921.42 (C-H Str), C≡C (no absortion). **^{1}H NMR (500 MHz, DMSO) :** 3.2-3.5 (1H, m), 2.2-2.4 (2H, t), 2.6-2.7 (3H, t), 2.4-2.6 (2H, m), 2.1 (S, 1H of Hydroxyl). **MASS :** 246 (M^+)**.**

Compound-4: 1-ethenyl-1-cyclohexanol dimer: Molecular formula: $C_{12}H_{18}O_2$, Molecular weight: 194.27. **FTIR (KBr) in cm^{-1}:** 3276.20 (O-H Str), 2856.86 (C-H Str), 2931.78 (Ar-H), C≡C (no absortion). **^{1}H NMR (500 MHz, DMSO) :** ($CDCl_3$) 1.42-2.23 (1H, m, cyclohexane-H), 7.23 (S, 1H of Hydroxyl). **MASS :** 195 (M^+)**.**

Compound-5: 3-methyl-1-pentyne-3-ol dimer: Molecular formula: $C_{10}H_{14}O_2$, Molecular weight: 166.21. **FTIR (KBr) in cm^{-1}:** 3441.07 (O-H Str), 2921.42 (C-H Str), C≡C (weak absortion). **^{1}H NMR (500 MHz, DMSO) :** 1.53-1.60 (2H, m), 1.61-1.63 (3H, d), 2.00 (S, 1H of Hydroxyl). **MASS :** 167 (M^+)**.**

Compound-6: 2-Phenyl-3-butyn-2-ol dimer: Molecular formula : $C_{16}H_{26}O_2$, Molecular weight : 250.37. **FTIR (KBr) in cm^{-1}:** 3329.17 (O-H Str), 2984.82 (C-H Str), 3062.69 (Ar-H), C≡C (weak absortion). **^{1}H NMR (500 MHz, DMSO) :** 7.23-7.6 (m, Ar-H), 1.92 (3H, S), 2.21 (S, 1H of Hydroxyl). **MASS :** 251 (M^+)**.**

RESULTS AND DISCUSSION

The dimer molecules (1-6) were synthesized by in presence of Cu(I)Cl in pyridine. In this method reactions were carried out and gave good yields (**Table 1**). All the synthesized compounds shown good antibacterial activity

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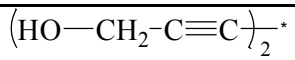
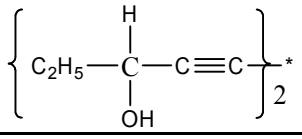
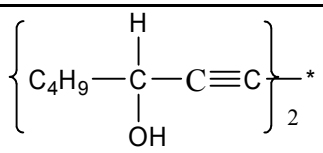
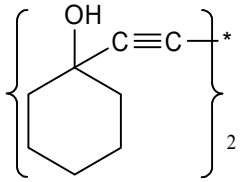
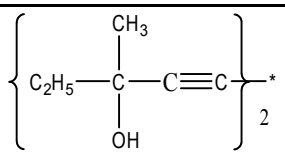
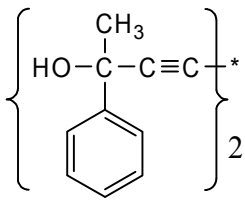
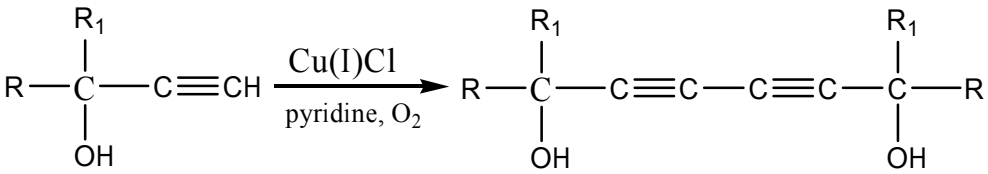
Table 1: Antibacterial activity of 1, 3-diyn–diols

S. No	Compound	Diameter of zone of Inhibition (mm)	
		S. aureus	*E. coli*
1	Propargyl alcohol dimer	8	14
2	1-Pentyne-3-ol dimer	12	17
3	1-octyne-3-ol dimer	11	9
4	1-ethenyl-1-cyclohexanol dimer	7	15
5	3-methyl-1-pentyne-3-ol dimer	13	9
6	2-Phenyl-3-butyn-2-ol dimer	14	12
7	Ampicillin	18	21

Table 2: Formation of 1, 3-diyn–diols

S. No.	R	R_1	Reaction Time (Hrs)	Product	Yield (%)
1	H	H	1.50		74
2	H	C_2H_5	1.42		91
3	H	C_4H_9	1.55		74
4	H	C_6H_{10}	1.28		72
5	CH_3	C_2H_5	1.35		89
6	CH_3	C_6H_5	2.10		76

Scheme 1: Dimerisation of alkynes in Glaser reaction condition



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