OPEN ACCESS INTERNATIONAL JOURNAL OF SCIENCE & ENGINEERING

Synthesis and Evaluation of Antioxidant Activities of 1,3-Diaryl-1H-pyrrazol-4-carbaldehydes

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Abstract: A new series of 1,3-Diaryl-1H-pyrrazol-4-carbaldehyde has been synthesized from hydrzone of aromatic ketone and phenyl hydrazine in presence of Vilsmear Hack reagent. The structures of synthesized compounds has been confirmed by elemental analysis FT-IR, 1H NMR, 13C NMR and mass spectral data. These synthesized compounds observed to show antioxidant activities by using DPPH method using ascorbic acid as standard.

Keywords: 1,3-Diaryl-1H-pyrrazol-4-carbaldehyde, Hydrzone, Vilsmear Hack reagent, Antioxidant activity

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I. INTRODUCTION

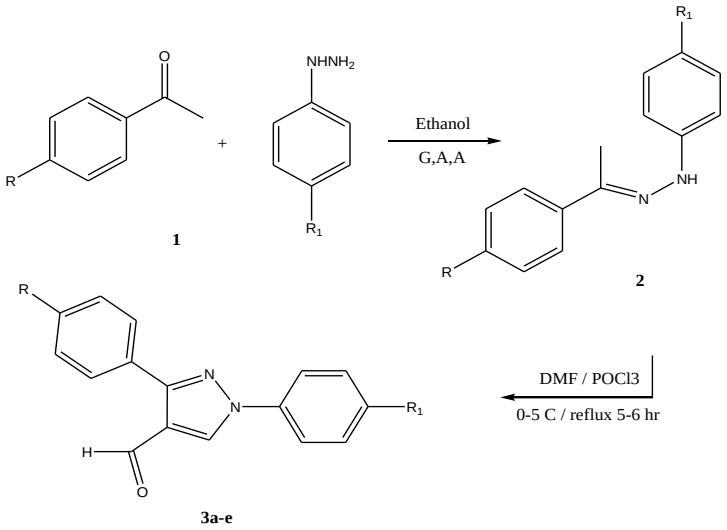
A pyrazole having remarkable pharmacological activities due to five member heterocyclic nitrogenous ring. Pyrazole are medicinally potent scaffold and exhibit broad spectrum of biological activities such as Anti-Inflammatory [1], Antimicrobial[2], Anticancer[3],

AntiHIV[4], Antioxident[5], Antipyratic[6], Antiviral[7] in pesticides pyrazole derivatives are effective against Tobacco Mosaic Virus which cause serious damage to plant[8], Acyl group at fourth position of pyrazole ring show Antifungi activity against Pythium aphanidermatum wich is a soil born pathogen and Rhizoctonia is a plant pathogenic fungus with a wide host range[9]

peethamber et al synthesized and revealed that some pyrazole derivatives show Antioxident and Antihyperglaycemic activity [10], Sharma et al synthesized and explained Antimicrobial activities of pyrazole[11], Alegaon et al synthesized and explained Anti-Inflametory Activity of Pyrazole derivatives[12], Selvam et al studied microvave assisted synthesis and Biological Activities of pyrazole[13], Shrivastava et al synthesized and studied Anti hypoglycemic activity[14].

A new series of 1,3-Diaryl-1H-pyrrazol-4-carbaldehyde has been synthesized from hydrazone of substituted phenyl hydrazine and substituted acetophenone by cyclization with Vilsmear Hack reagent. These newly synthesized compounds show antioxidant activity against.

Reaction Scheme:



1 **2** **3a-e**

R= -OH,-NO_2,-Cl R1= -Br,-CH_3

Experimental:

Chemicals, reagents and solvents were of analytical grade or of the highest quality commercially available. The chemicals were purchased from ACS Thermo Fischer and SDFL respectively, these solvents used were of analytical grade and purified before their use.

Preparation of Hydrazone(2) from substituted Acetophenone and Phenyl hydrazine

Hydrozone(**2**) were prepared by simple condensation of substituted

Acetophenone (0.01mole) with Substituted Phenyl hydrazine (0.01mole) in acidic medium. The reaction is monitored on TLC after completion of reaction, cool reaction mixture at room temperature and poured into ice cold water with constant stirring obtains a precipitate , filter it wash residue with cold water and recrystallized from Ethanol

Preparation of 1,3-Diaryl-1H-pyrrazol-4-carbaldehyde(3) from Hydrazone(2)

Hydrazone (12 mmol) was added to a cold solution of dimethylformamide (40.0 mmol) then Phosphorylchloride (40.0 mmol) was added and the resulting mixture was stirred at 60^0Cfor 6 h. The mixture was poured into ice-cold water. A saturated solution of potassium carbonate was added to neutralize the mixture; the solid precipitated was filter; washed with water; dried and recrystallized from ethanol.

3-(4-Hydroxyphenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde

(3a). Colorless solid powder; Yield: 60%; m.p.: 126–138^0C; IR (KBr, cm^{-1}): 2778 (CH of CHO), 1668 (C=O), 1628(C=C), 1568 (C=N). 1H NMR (400 MHz, d, ppm, , CDCl3): 7.42 (t, 1H, J = 7.1 Hz, Ar-H), 7.56 (t, 2H, J = 7.4 Hz, Ar-H), 7.70 (d, 2H, J = 8.4 Hz, Ar-H), 7.90 (d, 2H, J = 8.6 Hz, Ar-H), 7.94 (d, 2H, J = 8.2 Hz, Ar-H), 9.32 (s, 1H,pyrazole), 9.76 (s, 1H, CHO), 9.96 (s, 1H, OH).

3-(4-Nitrophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde

(3b). Light yellowish powder; Yield: 64%, m.p.:164–166^0 C; IR (KBr, cm^{-1}): 276 (CH of CHO), 1732 (C=O), 1630(C=C), 1566 (C=N). 1H NMR (400 MHz, d, ppm, , CDCl3): 7.44 (t, 1H, J = 7.0 Hz, Ar-H), 7.62 (t, 2H, J = 7.6 Hz, Ar-H), 7.89 (d, 2H, J = 8.4 Hz, Ar-H), 7.91 (d, 2H, J = 8.6 Hz, Ar-H) 7.94 (d, 2H, J = 8.2 Hz, ArAH) 9.18 (s, 1H, pyrazole), 9.80 (s, 1H, CHO).

3-(4-Chlorophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde

(3c) Colorless solid powder; Yield: 68%; m.p.: 125–127^0C; IR (KBr, cm^{-1}): 2756 (CH of CHO), 1672(C=O), 1639(C=C), 1552(C=N).678(C-Cl) 1H NMR (400 MHz, d, ppm, , CDCl3): 7.39 (t, 1H, J = 7.3 Hz, Ar-H), 7.62 (t, 2H, J = 7.6 Hz, Ar-H), 7.74 (d, 2H, J = 8.0 Hz, Ar-H), 7.76 (d, 2H, J = 8.4 Hz, Ar-H), 7.84(d, 2H, J = 7.8 Hz, Ar-H), 9.26 (s, 1H,pyrazole), 9.62 (s, 1H, CHO).

1-(4-Bromophenyl)-3-phenyl-1H-pyrazole-4-carbaldehyde

(3d) Yield: 74%; mp. 172–174^0C, IR (KBr cm^{-1}) :2771 (C–H in CHO), 1680 (C=O), 1570 (C=N) 1612(C=C), 662 (C–Br); 1H NMR (300 MHz, d ppm, CDCl3): 7.22 (t, 1H, J = 7.1 Hz, Ar-H), 7.48 (t, 2H, J = 7.4 Hz, Ar-H), 7.56 (d, 2H, J = 7.8 Hz, Ar-H), 7.68 (d, 2H, J = 7.4 Hz, Ar-H), 7.62(d, 2H, J = 7.2 Hz, Ar-H 8.92 (s, 1H, CHO),8.71 (s, 1H, Pyrazole).

1-(4-Methylphenyl)-3-diphenyl-1H-pyrazole-4-carbaldehyde

(3e) Yield 64%, mp. 166–168^0C; IR (KBr) cm^{-1}: 2748 (C–H of CHO), 1710 (C=O), 1524(C=N),1498 (C=C); 1H NMR (300 MHz, d ppm, CDCl3): 7.20 (t, 1H, J = 7.2 Hz, Ar-H), 7.56 (t, 2H, J = 7.2 Hz, Ar-H), 748 (d, 2H, J = 7.6 Hz, Ar-H), 7.66(d, 2H, J = 7.4 Hz, Ar-H), 7.48(d, 2H, J = 7.0 Hz, Ar-H 8.19(s, 1H, CHO), 7.78 (s, 1H, Pyrazole),

Biological Evaluation:

Antioxidant Activity

The synthesized 1,3-Diaryl-1H-pyrrazol-4-carbaldehyde show good to moderate activities against bacterial stain among them 3-(4-Chlorophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde have more zone of inhibition (%) as compared to other synthesized compounds of 1,3-Diaryl-1H-pyrrazol-4-carbaldehyde. we had taken biological activities of synthesized compounds that is antioxidant activities by using DPPH method.

The anti-oxidant activity of compounds can be determine by using the colorimetric DPPH assay, as described by Shimada et al284., (1992) to determine the radical scavenging activity of the synthesized compounds. In-vitro Antioxidant screening of synthesized compounds was done by using only DPPH method. This method chosen because it is fast, simple and accurate method. Moreover, the method can be applied to the sample in small quantities. DPPH is a purple organic compound and reacts with the antioxidant compound, DPPH would be reduced and its colour would be turned yellow.

The hydrogen donating capacity of test samples is quantified in terms of their ability to scavenge the relatively stable, organic free radical DPPH and by consequent reduction. The absorption of the deep violet DPPH solution is measured at 517 nm, after which absorption decreases due to decolorization to a yellow-white color, in the event of reduction. This decrease in absorption is stoichiometric according to the degree of reduction (Arulpriya et al.).

II.MATERIAL AND METHOD

Reagents Used

- Radical: DDPH
- Solvent: DMSO
- Standard: Ascorbic acid

Preparation of 0.3 Mm DPPH Solution

It was prepared by dissolving DPPH (5.91 mg) in 50 ml of ethanol. This stock solution was prepared freshly and kept in the dark at ambient temperature when not used.

Preparation of Sample Stock Solution

The sample stock solution was prepared by dissolving the compound in suitable solvent (DMSO) with a final concentration of 1 mg/ml.

Reparation of Standard Stock Solution

The standard stock solution was prepared by dissolving the Ascorbic acid in suitable solvent (DMSO) with a final concentration of 1 mg/ml.

Procedure

The free-radical scavenging activity was estimated by DPPH assay. The reaction mixture contained 10 µl of test sample and 190 µl of methanolic solution of 0.3 mM DPPH radical. The

mixture was then shaken vigorously and incubated at 37° C for 5 min. The absorbance was measured at 517 nm on ELISA plate reader indicated higher free radical scavenging activity (Awaley et al.), which was calculated using the following equation:

(%) Free radical scavenging effect =

$$\frac{[\text{Absorbance of control (Ac)} - \text{Absorbance of sample (As)}]}{\text{Absorbance of control (Ac)}} \times 100$$

Table 1:- DPPH radical scavenging activity of some titled compounds

Sr. No.	Sample Code	Antioxidant Potential (Mean ±SD)
1	Ia	26.442±2.058
2	Ib	45.851±2.631
3	Ic	-----
4	Id	-----
5	Ie	67.511±3.002
6	+Ve Control (Ascorbic acid)	89.781±3.232

III.CONCLUSION

From the above table 1 it is concluded that the screening of antioxidant activity performed compounds are compared with standard ascorbic acid and results were expressed as mean ± standard deviations. The results indicated that all these synthetic compounds have significant antioxidant activity, and among them compound **Ia, Ib and Ie** exhibited antioxidant potential. Rests of the compounds are not exhibiting antioxidant activities.

Conflict of Interest

Author has no conflict of interest**.**

IV.REFERENCES

[1] Nossier S Eman, Fahmy H Hoda, Khalifa M Nagy, El-Eraky I Wafaa, and Marawan A.Baset , Molecule, 22, 2017, 512

[2] Shijie Du, Zaimin Tian, Dongyan Yang, Xiuyun Li, Hong Li, Changqing Jia,Chuanliang Che, Mian Wang and Zhaohai Qin, Molecule,20,2015,8396-8408

[3] Cuili Chen, Jia Chen, Haiying Gu, Ning Bao and Hong Dai, Molecule,22,2017,1126

[4] Jordan W C, Drew C R, Natl. J. Med. Assoc.,88, 1996, 333.

[5] SharathV, Kumar H V, Naik N, J. Pharm. Res. 6, 2013, 785–790.

[6] CarmoMalvar D, FerreiraR.T, de Castro R A, de Castro L L, Freitas AC, Costa E A, Florentino I F, Mafra J C, de Souza G E, Vanderlinde F A, Life Sci.,95, 2014, 81–88.

[7] Yu LG, Ni T F, Gao W, He Y, Wang Y Y, Cui H W, Yang C G, Qiu W W, Eur. J. Med. Chem., 90, 2015, 10–20

[8] 8 Jin-Jing Xiao, Min Liao, Ming-Jie Chu, Zi-Li Ren, Xin Zhang, Xian-Hai Lv and Hai-Qun Cao, Molecule, 20, 2015, 808-820

[9] Amar Patil, Rahul Jadhav, Hemant Raundal, Lokesh Sharma, Rupali Badgujar and Vivek Bobade, J. Chem. Pharm. Res, 6(8), 2014, 218-223

[10] Alegaon S G, Alagawadi K R, Garg M K, Dushyant K, Vinod. Chem.,54, 2014, 51-59

[11] Sharma S, Bhatt H B, journal of Saudi chem..soc., 2013

[12] Alegaon S G, Alagawadi K R , Garg M K, Dushyant K. Vinod D, Bioorganic chemistry, 54,2014,51-59

[13] Selvam Theivendren P,Kumar Palanirajan V, Govindaraj Saravanan, Chinnasamy

Rajaram P,journal of Saudi chem..soc, 2012

[14] Shrivastva S K, Nirupan Das, Abhilasha Verma, Shrivastva P K , Indian Journal Chemistry, 47B, 2008, 1555-1558.

[15] M. G. Awaley , J. G. Nakade , Ankit S. Kale, Himanshu S. Jaiswal, Journal of Emerging Technologies and Innovative Research, 7(11), 102-111.