SYNTHESIS AND ANTIOXIDANT ACTIVITIES OF SOME ¹N-ACETYL-3-(3-HYDROXYPHENYL)-5-(SUBSTITUTED PHENYL)-4, 5-DIHYDRO-¹H-PYRAZOLINES

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ABSTRACT

A series containing sixteen titled pyrazoline derivatives have been synthesized by perchloric acid catalyzed cyclization cum acetylation of 3-hydroxyphenyl chalcones, hydrazine hydrate and acetic anhydride by refluxing condition. The yields of the synthesized ¹N-acetylpyrazolines were found to be more than 90%. These 1-acetylpyrazolines were characterized by their physical constants and spectral data. The antioxidant activities of these pyrazolines derivatives have been evaluated by 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity.

Keywords: *3-Hydroxyphenyl chalcones; ¹N-acetylpyrazolines; Perchloric acid; IR and NMR spectra.*

1. INTRODUCTION

Pyrazoline and its derivatives are important medicinal heterocycles containing two nitrogen atoms in the five-membered ring [1-3]. They possess many biological activities such as anti-bacterial [4], anti-fungal [5], anti-depressants [6], anti-convulsant [7], anti-inflammatory [8], anti-tumour [9], anaesthetic [10], analgesic [11], anti-cancer [12] MAO-B inhibitors [13], steroidal, nitric oxide synthase inhibitor, anti-viral and cannabinoid CBI receptor antagonists [8]. Many synthetic methods including solvent-free techniques were reported [1-3, 14] in the literature for synthesis of pyrazolines and its derivatives. Glacial acetic acid and acetic anhydride were employed with solvent assisted conventional heating, solvent-free microwave and ultrasound wave irradiation for acetylation of pyrazolines [15,16]. The sulfated solid catalysts such as sulphated titania [17], sulphated zirconia [18],

sulphated tin oxide [19], sulphated and molybdated iron oxide [20] and sulphated and phosphate zirconia [21] were employed for solvent assisted and solvent-free synthesis of organics methods. Osman et al. [22] have synthesised 75% yield of 4,7-dimethoxy-5-(5-aryl-N-acetylpyrazolin-3-yl) benzofuran-6-ols by refluxing of Khellinone chalcones, hydrazine hydrate and glacial acetic acid. Some novel 5-(4-tolyl)-4,5-dihydro-1-acetylpyrazol-3-yl-phenyl}-3H-quinazolin-4-ones were synthesized using refluxation method of corresponding chalcones with hydrazine acetic acid in ethanol by Mosaad et al. [23]. More than 84% yield of some series of new N1-cinnamoyl-3, 5-diaryl-2-pyrazolines have been synthesized using microwave as well as conventional heating by Srivastava et al. [16]. Shah et al., have synthesized 75% yield and studied the IR and ¹H NMR spectra of some new series of 4-(4-hydroxyphenyl)-3-chloro-1-{4-5-(substituted phenyl)-1-acetyl-4,5-dihydro-pyrazol-3-ylphenyl} azetidin-2-one

with 3-chloro-1-{4-5-(substituted phenyl)-4,5-dihydro-pyrazol-3-yl phenyl}-4-(4-hydroxyphenyl) azetidin-2-one in acetic acid [24]. N-acetyl-3-(2-naphthyl)-5-aryl pyrazoline derivatives were synthesized and studied their FTIR, NMR and HRMS data by Ethiraj et al. [25]. Many N-acetyl pyrazole derivatives such as N-acetyl-3,5-diphenyl pyrazolines [26], 1-acetyl-4-5-(3-chloro-4-fluorophenyl)-2-furyl-3-substituted phenyl-4,5-dihydro-1H-pyrazoles [27], 2,4-bis-(tetrahydro-1,4-oxazine)-6-4''-{1''-acetyl-5''-(4'''-methoxy phenyl)-2''-pyrazoline-3''-yl} phenylamino-s-triazine [28], fluorine containing aryl furyl N-acetyl pyrazolines [29] and 4,6-dimethoxy-5-(1-acetyl-5-aryl-2-pyrazolin-3-yl) benzofurans [20] were synthesized by synthetic organic chemists using conventional heating method and studied their spectral data. These 1-acetyl pyrazoline derivatives possess important biological activities such as antibacterial [16, 24, 27, 29-31], cytotoxicity [25], endogenous proteolysis [26], EGFR kinase [32] and anti-inflammatory activities [23]. The literature survey reveals that there is no information available for perchloric acid assisted cyclization and acetylation of 3-hydroxyphenyl chalcones for synthesis of ¹N-acetyl-3-(3-hydroxyphenyl)-5-(substituted phenyl)-4,5-dihydro-¹H-pyrazoline derivatives. Therefore the author have taken efforts to synthesize some ¹N-acetylpyrazolines including ¹N-acetyl-3-(3-hydroxyphenyl)-5-(substituted phenyl)-4,5-dihydro-¹H-pyrazoline derivatives by perchloric acid assisted cyclization of chalcones with hydrazine hydrate and acetic anhydride and evaluated the antioxidant activities by 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity. The purities of these pyrazolines were examined by their physical

constants and spectral data with reference published earlier in literature.

2. EXPERIMENTAL

2.1 GENERAL

All chemicals used were procured from Sigma-Aldrich and E-Merck. Melting points of all pyrazole-1-carbothioamides have been determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr, 4000-400 cm⁻¹) have been recorded on Bruker (Thermo Nicolet) Fourier transform spectrophotometer. The NMR spectra of all pyrazolines have been recorded on Bruker AV400 spectrometer operating at 400 MHz for recording ¹H and 100 MHz for ¹³C spectra in CDCl₃ solvent using TMS as internal standard. Mass spectra have been recorded on Shimadzu spectrometer using chemical ionization technique.

2.2 SYNTHESIS OF 3-HYDROXYPHENYL CHALCONES

Substituted styryl 3-hydroxyphenyl ketones were synthesized by method reported in literature [17].

2.3 SYNTHESIS OF ¹N-ACETYL-3-(3-HYDROXY PHENYL)-5-(SUBSTITUTED PHENYL)-4,5-DIHYDRO-¹H-PYRAZOLINES

A solution of 3-hydroxyphenyl chalcones (5 mmol) in 15 mL of acetic anhydride was added drop-wise to 0.6 mL of hydrazine hydrate (12.5 mmol). About 1 mL of perchloric acid was added to this mixture and refluxed for 15h (Scheme 1). The reaction mixture was poured in ice-cold water, obtaining the crude ¹N-acetylpyrazoline derivatives which were crystallized from ethanol. The analytical, physical constants and mass spectral fragments of ¹N-acetyl-3-(3-hydroxyphenyl)-5-(substituted phenyl)-4,5-dihydro-¹H-pyrazolines were presented in Table 1.

Scheme 1. Synthesis of ¹N-acetyl-3-(3-hydroxyphenyl)-5-(substituted phenyl)-4,5-dihydro-¹H-pyrazolinesTABLE 1: THE ANALYTICAL, PHYSICAL CONSTANTS AND MASS FRAGMENTS (M/Z) DATA OF ¹N-ACETYL-3-(3-HYDROXYPHENYL)-5-(SUBSTITUTED PHENYL)-4,5-DIHYDRO-¹H-PYRAZOLINES

Entry	X	Molecular Formula	M.W.	Yield (%)	m.p. (°C)	Mass(m/z)
1	H	C ₁₇ H ₁₆ N ₂ O ₂	280	93	122-123	280[M ⁺]
2	2-Br	C ₁₇ H ₁₅ BrN ₂ O ₂	359	92	203-204(201-203)[19]	359[M ⁺], 361[M ²⁺]
3	3-Cl	C ₁₇ H ₁₅ ClN ₂ O ₂	315	93	143-144	315[M ⁺], 317[M ²⁺]
4	4-Cl	C ₁₇ H ₁₅ ClN ₂ O ₂	315	90	189-190(187-189)[32]	315[M ⁺], 317[M ²⁺]
5	4-OCH ₂ CH ₃	C ₁₉ H ₂₀ N ₂ O ₃	324	92	155-156(153-155)[32]	324[M ⁺]
6	4-CH ₂ CH ₃	C ₁₉ H ₂₀ N ₂ O ₂	308	91	132-133(131-132)[32]	308[M ⁺]
7	2-F	C ₁₇ H ₁₅ FN ₂ O ₂	298	90	130-131(129-130)[32]	298[M ⁺], 300[M ²⁺]
8	3-F	C ₁₇ H ₁₅ FN ₂ O ₂	298	90	179-180(178-179)[32]	298[M ⁺], 300[M ²⁺]
9	2-OCH ₃	C ₁₈ H ₁₈ N ₂ O ₃	310	94	96-97(94-96)[32]	310[M ⁺]
10	4-OCH ₃	C ₁₈ H ₁₈ N ₂ O ₃	310	95	117-118	310[M ⁺]
11	4-CH ₃	C ₁₈ H ₁₈ N ₂ O ₂	294	93	145-146(144-145)[32]	294[M ⁺]
12	3-NO ₂	C ₁₇ H ₁₅ N ₃ O ₄	325	90	126-127	325[M ⁺]
13	4-NO ₂	C ₁₇ H ₁₅ N ₃ O ₄	325	90	138-139	325[M ⁺]
14	4- <i>t</i> -Bu	C ₂₁ H ₂₄ N ₂ O ₂	336	90	129-130(128-129)[32]	336[M ⁺]
15	2-Thienyl	C ₂₁ H ₁₈ N ₂ O ₂ S	362	91	185-186(183-184)[32]	362M ⁺
16	3,4,5-(OCH ₃) ₃	C ₂₀ H ₂₅ N ₂ O ₅	370	93	163-164(161-162)[32]	370M ⁺

2.4. MEASUREMENT OF ANTIOXIDANT ACTIVITY

The DPPH radical scavenging activity technique [30, 31] was utilized for the measurement of antioxidant activity of all prepared methanones. About 20 mL of sodium acetate buffer solution was prepared by dissolving 1.64 g of sodium acetate in 15 mL of water and 150 μL of acetic acid, and

the final volume was adjusted to 20 mL of water. About 50 mL of 0.2 mmol DPPH solution was prepared by dissolving 3.9 g of DPPH in 50 mL of ethanol. About 10 mL of α-tocopherol solution was prepared by dissolving 1 mg of α-tocopherol in 10 mL of ethanol. About 1.0 mL of buffer solution was mixed with 0.5 mL of DPPH

solution in the test tubes and arranged serially. The test solution and α -tocopherol solution were added to the test tubes and kept aside for 30 minutes at room temperature. The absorbance was measured on an UV-Vis spectrophotometer (Shimadzu-1650) at 517 nm. Mixture of sodium acetate buffer and ethanol was used as the reference. The plot was made with the quantity of the compound versus absorption and the IC_{50} values were determined. The antioxidant activity was expressed in terms of IC_{50} ($\mu\text{g/mL}$, concentration required to inhibit DPPH radical formation by 50%). α -tocopherol was taken as a positive control. The radical scavenging activity was calculated as: DPPH radical scavenging activity (% of inhibition) =

$$\frac{\text{Control absorbance} - \text{Sample absorbance}}{\text{Control absorbance}} \times 100$$

3. RESULTS AND DISCUSSION

In our research lab, the authors attempted to synthesize 1N -acetyl substituted pyrazoline derivatives by cyclization of 3-hydroxyphenyl chalcones possess electron with-drawing as well as electron donating group as substituents, hydrazine hydrate, ethanol and acetic anhydride in the presence of perchloric acid catalyst under reflux condition. Hence the author have synthesized the 1N -acetyl substituted pyrazoline derivatives by the cyclization of 2 mmol of 3-hydroxy phenyl chalcone (entry 1), 2 mmol of hydrazine hydrate, 1 mmol of acetic anhydride, 20 mL of ethanol and 1 mL of perchloric acid under refluxation for 15h. During the course of this reaction perchloric acid catalyses cyclization cum acetylation between chalcones, hydrazine hydrate and acetic anhydride through elimination of water followed by proton transfer gave the 1N -acetylpyrazolines.

The yield of the 1N -acetylpyrazolines in this reaction is more than 90%. The chalcone containing electron donating substituent (OCH₃) gave higher yields than electron-withdrawing (halogens, NO₂) substituents. Further we have investigated this cyclization reaction with an equi-molar quantities of the styryl 3-hydroxyphenyl ketone (2 mmol) (entry1), hydrazine hydrate and 1 mmol of acetic anhydride under the same condition as above. In this reaction the obtained yield was 93% (Scheme 1). The effect of catalyst on this reaction was studied by varying the catalyst quantity from 0.2 to 2 mL. As the catalyst quantity is increased from 0.2 to 1 mL, the percentage yield of product is increased from 88 to 93%. Further increase in the catalyst amount beyond 1 mL, there is no significant increase in the percentage of the product. The optimum quantity of catalyst loading was found to be 1 mL. The effect of solvents on the yield was also studied with methanol, ethanol, dichloromethane and tetrahydrofuran from each component of the catalyst (entry 1). The effect of catalyst loading is shown in Figure 1.

Fig. 1. The effect of catalyst loading

The effect of solvents on the yield of 1N -acetylpyrazolines was presented in Table 2. From the table, the highest yield of 1N -acetylpyrazolines is obtained from the cyclization cum acetylation of chalcone,

hydrazine hydrate and acetic anhydride with perchloric acid in ethanol medium.

TABLE 2: THE EFFECT OF SOLVENT ON THE YIELD OF THE ¹N-ACETILPYRAZOLINES(1).

EtOH	MeOH	DCM	Dioxane	THF
93	86	87	87	85

EtOH: Ethanol; MeOH: Methanol; DCM: Dichloro-methane; THF: Tetrahydrofuron
The infrared and NMR spectroscopic data of selective compounds are summarized below:

¹N-acetyl-3-(3-hydroxyphenyl)-5-phenyl-4,5-dihydro-¹H-pyrazolines (1): IR (ν, 4000-400cm⁻¹); 3547 (OH), 1666 (CO), 1583 (CN); ¹H NMR (CDCl₃, 400MHz, ppm) δ = 2.491 (s, 3H, CH₃), 3.013(dd, 1H, H₄, J=16.6), 3.717 (dd, 1H, H₄, J=16.6), 5.573 (dd, 1H, H₅, J=18.3), 6.891-7.236 (m, 9H, Ar-H); ¹³C NMR (CDCl₃, 100MHz, ppm) δ=168.09 (CO), 23.46 (CH₃), 158.46 (CN), 122.37-137.26 (Ar-C).

¹N-acetyl-3-(3-hydroxyphenyl)-5-(3-chlorophenyl)-4, 5-dihydro-¹H-pyrazolines (3): IR (ν, 4000-400cm⁻¹); 3548 (OH), 1678 (CO), 1589 (CN); ¹H NMR (CDCl₃, 400MHz, ppm) δ = 2.489 (s, 3H, CH₃), 3.197 (dd, 1H, H₄, J=15.3), 3.792 (dd, 1H, H₄, J=15.3), 5.631 (dd, 1H, H₅, J=16.3), 6.830-7.023 (m, 9H, Ar-H); ¹³C NMR (CDCl₃, 100MHz, ppm) δ = 170.65 (CO), 24.54 (CH₃), 156.87 (CN), 124.12-148.36 (Ar-C).

¹N-acetyl-3-(3-hydroxyphenyl)-5-(4-methoxyphenyl)-4,5-dihydro-¹H-pyrazolines (10): IR (ν, 4000-400cm⁻¹); 3534 (OH), 1663 (CO), 1586 (CN), 1423 (C-O-C); ¹H NMR (CDCl₃, 400MHz, ppm) δ = 2.354 (s, 3H, CH₃), 3.021 (dd, 1H, H₄, J=15.8), 3.695 (dd, 1H, H₄, J=15.8), 5.543 (dd, 1H, H₅, J=15.4), 6.210-7.351 (m, 9H, Ar-H), 3.785 (s, 3H, OCH₃); ¹³C NMR (CDCl₃,

100MHz, ppm) δ = 176.98 (CO), 24.03 (CH₃), 158.02 (CN), 123.57-147.29 (Ar-C), 68.25 (OCH₃).

¹N-acetyl-3-(3-hydroxyphenyl)-5-(3-nitrophenyl)-4,5-dihydro-¹H-pyrazolines (12): IR (ν, 4000-400cm⁻¹); 3554 (OH), 1676 (CO), 1590 (CN); ¹H NMR (CDCl₃, 400MHz, ppm) δ= 2.699 (s, 3H, CH₃), 3.617 (dd, 1H, H₄, J=16.4), 3.991 (dd, 1H, H₄, J=16.4), 5.923 (dd, 1H, H₅, J=15.9), 6.893-7.543 (m, 9H, Ar-H); ¹³C NMR (CDCl₃, 100MHz, ppm) δ= 170.98 (CO), 24.93 (CH₃), 158.96 (CN), 124.39-148.34 (Ar-C).

¹N-acetyl-3-(3-hydroxyphenyl)-5-(4-nitrophenyl)-4,5-dihydro-¹H-pyrazolines (13): IR (ν, 4000-400cm⁻¹); 3558 (OH), 1679 (CO), 1596 (CN); ¹H NMR (CDCl₃, 400MHz, ppm) δ= 2.706 (s, 3H, CH₃), 3.643 (dd, 1H, H₄, J=16.0), 3.878 (dd, 1H, H₄, J=16.0), 5.990 (dd, 1H, H₅, J=15.3), 6.809-7.562 (m, 9H, Ar-H); ¹³C NMR (CDCl₃, 100MHz, ppm) δ = 171.09 (CO), 24.99 (CH₃), 158.98(CN), 122.94-146.28 (Ar-C).

3.1 ANTIOXIDANT ACTIVITY

From the experimental statistical results, the observed antioxidant activities of methanones were presented in Table 3. From Table 3, all compounds showed good antioxidant activity referred with standard. The observed percentages of inhibition of DPPH radical scavenging activities are 35.11-37.61 and the standard value is 37.48. Among all pyrazolines, the methoxy substituted pyrazolines (9, 10 and 16) were shown excellent antioxidant activity. Pyrazolines 5 and 14 are showed good antioxidant activity.

TABLE 3. ¹N-ACETYL-3-(3-HYDROXYPHENYL)-5-(SUBSTITUTED PHENYL)-4,5-DIHYDRO-¹H-PYRAZOLINES

Entry	X	Antioxidant activity (DPPH radical scavenging)
1	H	35.18±1.58
2	2-Br	35.99±1.23
3	3-Cl	35.69±1.68
4	4-Cl	35.35±1.92
5	4-OCH ₂ CH ₃	37.18±1.09
6	4-CH ₂ CH ₃	35.25±1.14
7	2-F	35.61±1.00
8	3-F	35.12±1.07
9	2-OCH ₃	37.01±1.18
10	4-OCH ₃	37.52±1.09
11	4-CH ₃	35.11±1.21
12	3-NO ₂	35.45±1.21
13	4-NO ₂	35.12±1.51
14	4- <i>t</i> -Bu	37.08±1.19
15	2-Thienyl	35.22±1.33
16	3,4,5-(OCH ₃) ₃	37.61±1.19
Std	α -Tocopherol	37.49±1.02

4. CONCLUSIONS

A series of sixteen ¹N-acetyl-3-(3-hydroxyphenyl)-5-(substituted phenyl)-4,5-dihydro-¹H-pyrazolines have been synthesized by perchloric acid catalyzed cyclization cum acetylation of 3-hydroxyphenyl chalcones, hydrazine hydrate and acetic anhydride. The observed yield of the product is more than 95%. These pyrazolines were characterized by their physical constants and spectroscopic data. The antioxidant activities of these pyrazolines were measured using DPPH radical scavenging activity. The methoxy substituted compounds showed excellent antioxidant activity and the alcoholic substituted pyrazolines shows good antioxidant activity.

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التخليق والأنشطة المضادة للأكسدة لبعض N1-أسيتيل-3- (3-هيدروكسي فينيل) 5- (فينيل تبديلي) -4، 5- داي هيدرو-1 H - 1 بارازولين

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الملخص:

تم تخليق سلسلة معنونه تحتوي على 16 من مشتقات بارازولين من حامض البيروكلوريك والمحفزة دوريا من أسئلة 3-هيدروكسي فينيل- الجالكونات ، هيدرات الهيدرازين وأنهيدريد الخليك الناتج من راجع التكتيف. نواتج تخليق N1-أسيتيل بارازولين وجد أنها أكثر من 90%. تم تحديد خصائص 1 أسيتيل بارازولين بواسطة الثوابت الفيزيائية والبيانات الطيفية. تم تقييم الأنشطة المضادة للأكسدة لمشتقات بارازولين باستخدام النشاط الذري الجذري (DPPH).