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Synthesis, spectral studies and antimicrobial activities of some 2-naphthyl pyrazoline derivatives

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ABSTRACT

A series of 2-naphthyl pyrazolines were synthesized by the cyclization of 2-naphthyl chalcones and phenylhydrazine hydrochloride in the presence of sodium acetate. The yields of pyrazoline derivatives are more than 80%. The synthesized pyrazolines were characterized by their physical constants, IR, ^{1}H, ^{13}C and MS spectra. From the IR and NMR spectra the C=N (cm^{-1}) stretches, the pyrazoline ring proton chemical shifts (ppm) of δ_{H_a}, H_b and H_c and also the carbon chemical shifts (ppm) of δC=N are correlated with Hammett substituent constants, *F* and *R*, and Swain–Lupton's parameters using single and multi-regression analyses. From the results of linear regression analysis, the effect of substituents on the group frequencies has been predicted. The antimicrobial activities of all synthesized pyrazolines have been studied.

Introduction

Pyrazoline refers to both the classes of simple aromatic ring organic compounds of the heterocyclic series characterized by a 5-membered ring structure composed of three carbon atoms and two nitrogen atoms in adjacent positions, and the unsubstituted parent compound. So these compounds with pharmacological effects on humans, they are classified as alkaloid, although they are rare in nature. Many pyrazolines show various pharmacological properties [1]. Some pyrazoline derivatives are used as pesticides [2], fungicides [3], antibacterial [4], antifungal [5], antiamoebic [6], and antidepressant activity [7] and insecticides. Heterocyclic of the type 3-hetaryl-1H-4,5-dihydropyrazoles arouse particular interest because the properties determined by the pyrazoline fragment are combined with the features of the corresponding hetarene [7,8]. Therefore, it should be noted that 3-(4-hydroxy-3-coumarinyl)-1H-4,5-dihydropyrazoles are structural analogues of 3-substituted 4-hydroxy-coumarins some representatives of which are effective blood anticoagulants. The pyrazoline function is quite stable, and has inspired chemists to utilize the mentioned stable fragment in bioactive moieties to synthesize new compounds possessing biological activity. Some related compounds were evaluated for anticonvulsant activity [9]. The antidepressant activity of these compounds was evaluated by the "Porsolt Behavioural Despair Test" on Swiss-Webster mice [10]. The α,β-unsaturated ketones can play the role of versatile precursors in the synthesis of the corresponding pyrazoline derivatives [11,12]. The reaction of hydrazine and its derivatives with α,β-unsaturated ketones and α,β-epoxy ketones is one of the preparative methods for the synthesis of pyrazolines and pyrazoles [13]. Alternatively, the reaction of substituted hydrazines with α,β-unsaturated ketones has been reported to form regioselective pyrazolines [14]. The synthesis of pyrazoline rings from chalcone derivatives containing anisole and the 3,4-methylenedioxyphenyl ring by the conventional method using acetic acid was reported with low yields [15]. Some 1-(4-arylthiazol-2-yl)-3,5-diaryl-2-pyrazoline derivatives have been synthesized by the reaction of 1-thiocarbamoyl-3,5-diaryl-2-pyrazoline derivatives with phenacetylbromide in ethanol. The structural elucidations of the compounds were performed by IR, ^{1}HNMR and mass spectral data and elemental analysis [16]. Semicarbazide (hydrochloride) and thiosemicarbazide on reaction with α,β-unsaturated ketones of the ferrocene series in excess of *t*-But-OK gave 1-carbamoyl and 1-thiocarbamoyl (ferrocenyl)-4,5-dihydropyrazoles. Ten new fluorine-containing 1-thiocarbamoyl-3,5-diphenyl-2-pyrazolines have been synthesized in 80–85% yields by a microwave-promoted solvent-free condensation of 2,4-dichloro-5-fluoro chalcones with thiosemicarbazide over potassium carbonate[17]. Nanoparticles of 1-phenyl-3-naphthyl-5-(dimethylamino phenyl)-2-pyrazolines ranging from tens to hundreds of nanometres have been prepared by the reprecipitation method [18]. Five new 1,3,5-triphenyl-2-pyrazolines have been synthesized by reacting 1,3-diphenyl-2-propene-1-one with phenylhydrazine hydrochloride and another five new 3-(2″-hydroxy naphthalen-1″-yl)-1,5-diphenyl-2-pyrazoline have been synthesized by reacting 1-(2′-hydroxylnaphthyl)-3-phenyl-2-propene-1-one with

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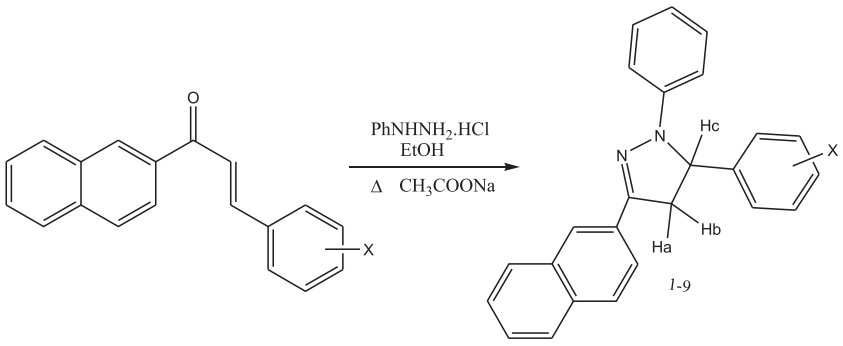

Where X= H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OCH_3, 4-CH_3

Scheme 1. Synthesis of 1-phenyl-3-(2-naphthyl)-5-(substituted phenyl)-2-pyrazolines.

Table 1
Analytical and mass spectral data of 1-phenyl-3-(2-naphthyl)-5-(substituted phenyl)-2-pyrazolines.

Entry	X	Mol. formula	Mol. weight	Yield (%)	m.p. (°C)	Mass (*m*/*z*)
1	H	$C_{25}H_{20}N_2$	348	85	116–117	348[M^+], 272, 271, 195, 181, 168, 167, 154, 147, 127, 77, 68, 41
2	3-Br	$C_{25}H_{19}BrN_2$	426	80	64–65	426[M^+], 428[M^{2+}], 299, 271, 155, 154, 145, 127, 79, 77
3	4-Br	$C_{25}H_{19}BrN_2$	456	85	110–111	426[M^+], 428[M^{2+}], 299, 271, 194, 168, 154, 145, 127, 77
4	2-Cl	$C_{25}H_{19}ClN_2$	382	83	81–82	382[M^+], 384[M^{2+}], 347, 271, 195, 154, 111, 77, 68, 35
5	3-Cl	$C_{25}H_{19}ClN_2$	382	83	91–92	382[M^+], 384[M^{2+}], 346, 271, 197, 195, 154, 145, 77, 68, 43, 35
6	4-Cl	$C_{25}H_{19}ClN_2$	382	87	62–63	382[M^+], 384[M^{2+}], 345, 270, 197, 195, 155, 154, 145, 77, 68, 35, 28
7	4-F	$C_{25}H_{19}FN_2$	366	80	65–66	366[M^+], 368[M^{2+}], 347, 289, 244, 239, 163, 155, 127, 122, 95, 77, 41, 28, 18
8	2-OCH_3	$C_{26}H_{21}N_2O$	378	85	104–105	378[M^+], 347, 301, 271, 251, 225, 145, 127, 107, 105, 91, 77, 31, 27
9	4-CH_3	$C_{26}H_{21}N_2$	362	85	70–71	362[M^+], 347, 285, 271, 257, 235, 195, 167, 165, 127, 91, 77, 28

Table 2
IR and NMR spectral data of 1-phenyl-3-(2-naphthyl)-5-(substituted phenyl)-2-pyrazolines.

Entry	X	*ν*CN (cm^{-1})	δ_{H_a} (ppm)	δ_{H_b} (ppm)	δ_{H_c} (ppm)	*δ*CN (ppm)
1	H	1671.38	3.286	3.954	5.333	153.01
2	3-Br	1590.34	3.254	3.960	5.290	169.77
3	4-Br	1677.78	3.253	3.955	5.303	153.14
4	2-Cl	1681.12	3.187	4.082	5.705	159.07
5	3-Cl	1683.12	3.248	3.962	5.278	152.81
6	4-Cl	1677.88	3.243	3.963	5.316	153.16
7	4-F	1678.88	3.253	3.953	5.319	153.10
8	2-OCH_3	1596.70	3.252	3.906	5.294	159.07
9	4-CH_3	1681.12	3.256	3.935	5.304	153.26

phenylhydrazine hydrochloride [19]. Also some new 1,3,5-triphenyl-2-pyrazolines have been synthesized by reacting 1,3-diphenyl-2-propene-1-one with phenylhydrazine hydrochloride and another five new 3-(2″-hydroxy naphthalen-1″-yl)-1,5-diphenyl-2-pyrazoline have been synthesized by reacting 1-(2′-hydroxylnaphthyl)-3-phenyl-2-propene-1-one with phenylhydrazine hydrochloride [20]. The effect of substituents on the group frequencies have been studied, through UV–vis, IR, ^1H and ^{13}C NMR spectra of ketones [21] unsaturated ketones [22–24], acid chlorides [14] acyl bromides, and their esters [25]. The effect of substituents on the infrared, proton and carbon-13 group frequencies of pyrazoline derivatives are not been studied so far. Hence the authors have taken efforts to synthesise some 2-naphthyl pyrazoline derivatives by cyclization of 2-naphthyl chalcones and phenylhydrazine hydrochloride in the presence of anhydrous sodium acetate and to study the spectral linearity and also the antimicrobial activities.

Experimental

All chemicals used were procured from Sigma–Aldrich and E-Merck. Melting points of all pyrazoles 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 JEOL-400 spectrometer operating at 400 MHz for recording ^1H spectra and 100 MHz for ^{13}C spectra in $CDCl_3$ solvent using TMS as internal standard. Mass spectra have been recorded on SHIMADZU spectrometer using chemical ionization technique.

Synthesis of 2-naphthyl pyrazolines derivatives: [1-phenyl-3-(2-naphthyl)-5-(substituted phenyl)-2-pyrazolines]

An appropriate equi-molar quantities of substituted styryl 2-naphthyl ketones (0.20 mmol), phenylhydrazine hydrochloride (0.20 mmol) and anhydrous sodium acetate (0.5 g) was refluxed [26] in (15 mL) ethanol for 8 h (Scheme 1). The completion of the reaction was monitored by TLC. The reaction mixture was cooled, and poured into ice cold water. The precipitate was filtered, dried and subjected to column chromatography using hexane and ethyl acetate (3:1) as eluent. The analytical and mass spectral data are presented in Table 1. The IR and NMR spectral data are given in Table 2.