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Synthesis of Some New Spiroindoline Derivatives Incorporated with Pyrazoloheterocycles

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ABSTRACT

Indole-2,3-dione (1) was treated with malonic acid (2) in a mixture of ethanol/pyridine to afford 1-[3-(2-oxoindolinylidene)]acetic acid (3). Compound 3 reacted with thionyl chloride to give the corresponding acid chloride (4). The acid chloride 4 reacted with arenes in the presence of $AlCl_3$ to yield 3-(2-oxoindolinylidene)acetophenones **5a–c**. *Compounds* **5a–c** *reacted with 3-methylpyrazolin-5-one derivatives* **6a,b** *to give 3-aracyl-3-[4'-(3'-methylpyrazolin-5-onyl)]-indoline-2-one derivatives* **7a–f**. *Compounds* **7a–f** *were treated with phosphorus pentoxide in phosphoric acid, with ammonium acetate or methanolic methylamine and with phosphorus pentasulfide to give spiro[indoline-3,4'-(pyrazolo[4,5-b]pyran)]-2-ones* **8a–f**, *spiro[indoline-3,4'-(pyrazolo[4,5-b]-dihydropyridine)]-2-ones* **9a–f**, **10a–f** *and spiro[indoline-3,4'-(pyrazolo[4,5-b]thiopyran)]-2-ones* **10a–f**, *respectively. All of the synthesized spiroheterocycle derivatives were identified by conventional spectroscopic methods (IR, ^1H NMR) and elemental analyses.* © *1996 John Wiley & Sons, Inc.*

INTRODUCTION

Certain spiro derivatives have shown antihyperglycemic [1], anticancer [2], antiinflammatory [3], and central nervous system activity [4]; also antibiotic aranorosim has been reported [5]. Some spiro compounds were used in the form of electron-donating colorless dyes [6]. Also, neuroleptic 2-substituted perhydro-1H-pyrido[1,2-a]pyrazines were prepared [7]. The syntheses of spiroheterocycles were carried out as reported in the literature [8–13]. The synthesis of methylene cyclopentenones that are analogous to the methylenomycin class of antibiotics has been reported [14]. Spiroheterocycles were prepared to be used as intermediates for aldose reductase inhibitors [15]. Recent literature reports revealed the synthesis of some new spiroheterocycles that have activity as herbicides and pesticides [16]. Photo and thermochromic properties of spiro derivatives have been studied [17]. Electronic and spectroscopic properties of spirocyclic compounds have been investigated [18,19]. Kinetic studies of solvent and pressure effects on thermal isomerization of spiro derivatives [20], studies of light-induced changes of the molecular charge in spironaphthoxazine compounds [21,22], and electrochemical studies on nitrospiro[indoline-naphthopyran] and 9,9'-spirobifluorene derivatives have been [23,24] investigated. Also, divers biological activities have been encountered in compounds having the indole ring system [25–28].

From all of the forgoing facts, together with the importance of the pyrazole derivatives [29–34], and as a continuation of our previous work [35–37], we report herein the synthesis of some new spiro-[indoline-3-pyrazoloheterocycles]-2-one derivatives.

RESULTS AND DISCUSSION

The synthesis of spiro(1,2-benzisothiazole-3(2H)-5'-oxazolidine)-2',4'-dione1,1-dioxides for use as antihyperglycemic agents has been achieved [1], and the

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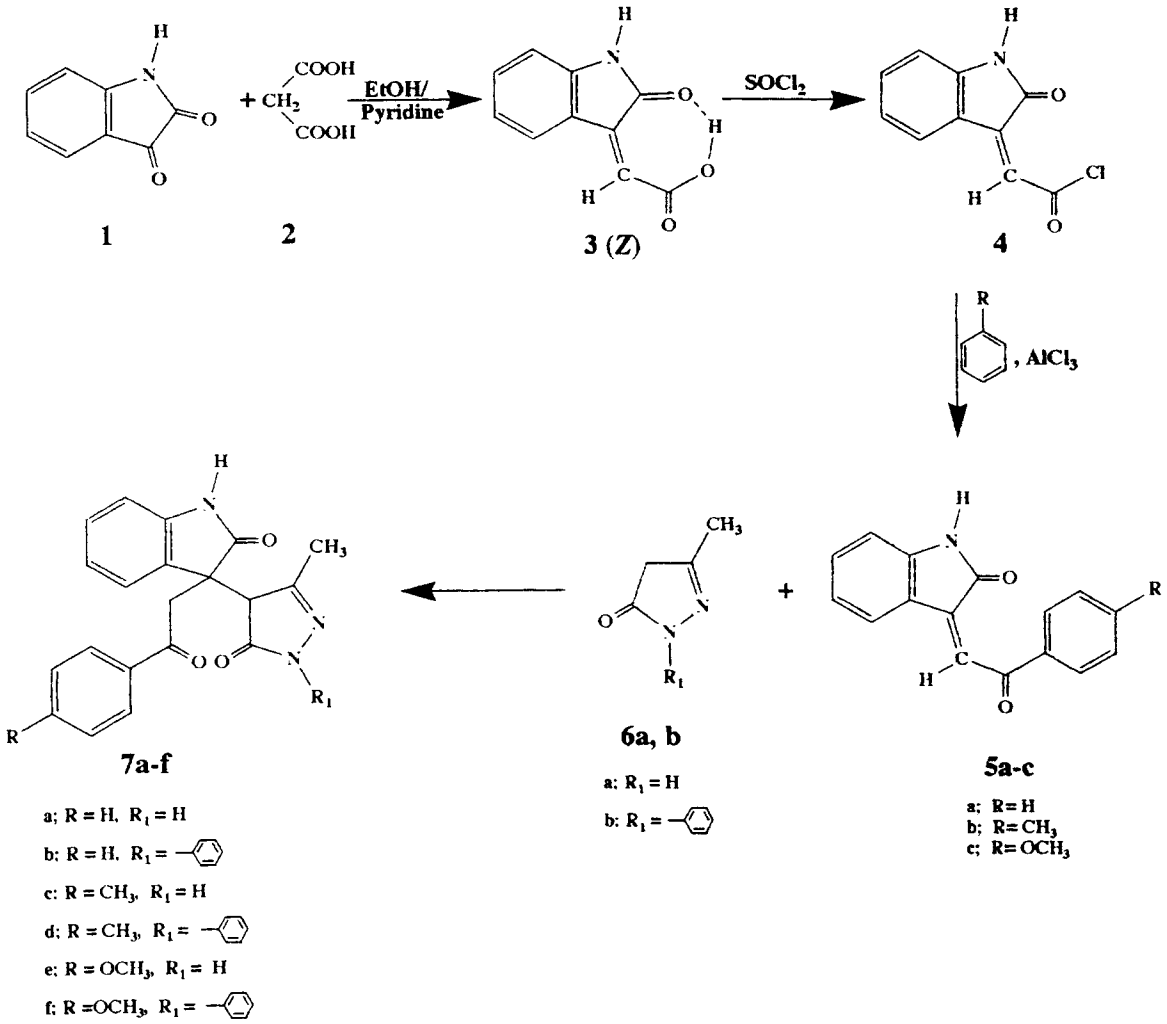
synthesis of a pentacyclic model of ptilomycalin A has been carried out [12]. The synthesis of compounds analogous to the methylenomycin class of antibiotics [14] has gained some importance. In some cases, the preparations of the biologically active spiro derivatives required many steps [38,39].

We report herein a facile synthesis of some new spiro[indoline-3-pyrazoloheterocycles]-2-one derivatives analogous to spiro[indan-1,1-[1H]-3-benzazepine] derivatives [38] and fredericamycin A [39]. The advantages of our syntheses were the use of inexpensive precursors and the facile occurrence of reactions using readily available reagents, and simple techniques.

Our syntheses started with the reaction of indole-2,3-dione (**1**) with malonic acid (**2**) to yield (Z)-1-[3-(2-oxoindolinylidine)]acetic acid (**3**). Compound **3** reacted with thionyl chloride to give the acid chloride **4**. Reaction of **4** with arenes in the presence of aluminum chloride gave 3-(2-oxoindolinylidene)acetophenones **5a–c** (Scheme 1). The structures of compounds **3**, **4**, and **5a–c** were established from their elemental analyses and spectroscopic data [36]. For the syntheses of the new target spiro[indoline-3-pyrazoloheterocycles]-2-one derivatives, compounds **5a–c** were treated with 3-methylpyrazolin-5-ones **6a,b** to yield 3-aracyl-3-[4′-(3-methylpyrazolin-5-onyl)]indoline-2-one derivatives **7a–f** [9,11]. The structures of compounds **7a–f** were elaborated from their elemental analyses and spectroscopic data (Table 1). The IR spectrum of **7a** showed characteristic strong absorption bands at 3200–3100 cm^{-1} corresponding to the stretching vibration of the NH group of the pyrazoline and indole ring, 3050 cm^{-1} for aromatic carbon–hydrogen stretching, 2950 cm^{-1} for aliphatic carbon–hydrogen, and 1680, 1710 cm^{-1} for carbonyl group stretching. The ^1H NMR spectrum of **7a** (CF_3COOH) showed the following signals: δ 2.25 (3H, s) for the methyl group of the pyrazoline moiety, 4.50 (2H, s) for the methylene protons of the phenacyl residue, 5.80 (1H, s) for the proton at C_4 of the pyrazoline



SCHEME 1

TABLE 1 Physical Data of 3-Phenacyl-3-[4′-(3′-methylpyrazolin-5′-onyl)]indoline-2-ones **7a–f** and Spiro[indoline-3-pyrazoloheterocycles]-2-one derivatives **8a–f**, **9a–f**, **10a–f**, and **11a–f**

Compound No.	Yield (%)	MP (°C)	Molecular Formula[a] (solvent of Crystallization)	IR (KBr), cm^{-1}	^1H NMR (CF_3COOH), δ(TMS)
7a	60	340–342	$C_{20}H_{17}N_3O_3$ (ethanol)	3200 (NH), 3050 (CH arom.), 2950 (CH aliph.), 1680, 1710 (C=O)	2.25 (3H, s), 4.50 (2H, s), 5.80 (1H, s), 7.00–7.70 (9H, m), 8.80 (2H, s)
7b	62	260–262	$C_{26}H_{21}N_3O_3$ (ethanol)	3200 (NH), 3060 (CH arom.), 2890 (CH aliph.), 1680, 1710 (C=O)	2.25 (3H, s), 4.60 (2H, s), 5.90 (1H, s), 7.00–7.70 (14H, m), 8.90 (1H, s)
7c	60	300–302	$C_{21}H_{19}N_3O_3$ (ethanol)	3200–3150 (NH), 3060 (CH arom.), 2870 (CH aliph.), 1680, 1710 (C=O)	2.25 (3H, s), 2.30 (3H, s), 4.50 (2H, s), 5.80 (1H, s), 7.00–7.70 (8H, m), 8.90 (2H, s)
7d	62	222–224	$C_{27}H_{23}N_3O_3$ (methanol)	3200 (NH), 3050 (CH arom.), 2890 (CH aliph.), 1680, 1710 (C=O)	2.26 (3H, s), 2.30 (3H, s), 4.60 (2H, s), 5.80 (1H, s), 7.00–7.70 (13H, m), 8.90 (1H, s)
7e	60	>350	$C_{21}H_{19}N_3O_4$ (ethanol)	3220 (NH), 3050 (CH arom.), 2890 (CH aliph.), 1685, 1710 (C=O)	2.27 (3H, s), 3.20 (3H, s), 4.50 (2H, s), 5.80 (1H, s), 7.00–7.75 (8H, m), 8.80 (2H, s)
7f	65	>350	$C_{27}H_{23}N_3O_4$ (methanol)	3220 (NH), 3050 (CH arom.), 2890 (CH aliph.), 1685, 1710 (C=O)	2.25 (3H, s), 3.20 (3H, s), 4.50 (2H, s), 5.80 (1H, s), 7.00–7.75 (13H, m), 8.80 (1H, s)
8a	61	155–157	$C_{20}H_{15}O_2N_3$ (ethanol)	3200 (NH), 3060 (CH arom.), 2890 (CH aliph.), 1705 (C=O)	2.28 (3H, s), 6.40 (1H, s), 7.00–7.80 (9H, m), 8.80 (2H, s)
8b	55	170–172	$C_{26}H_{19}O_2N_3$ (ethanol)	3210 (NH), 3060 (CH arom.), 2880 (CH aliph.), 1685 (C=O)	2.25 (3H, s), 6.50 (1H, s), 7.00–7.80 (14H, m), 8.80 (1H, s)
8c	59	150–152	$C_{21}H_{17}N_3O_2$ (methanol)	3220 (NH), 3050 (CH arom.), 2890 (CH aliph.), 1690 (C=O)	2.25 (3H, s), 2.30 (3H, s), 6.80 (1H, s), 7.00–7.80 (8H, m), 8.80 (1H, s)
8d	57	180–182	$C_{27}H_{21}N_3O_2$ (ethanol)	3200 (NH), 3060 (CH arom.), 2890 (CH aliph.), 1690 (C=O)	2.25 (3H, s), 2.30 (3H, s), 6.40 (1H, s), 7.00–7.80 (13H, m), 8.90 (1H, s)
8e	55	180–182	$C_{21}H_{17}N_3O_3$ (ethanol)	3200–3150 (NH), 3090 (CH arom.), 2890 (CH aliph.), 1690 (C=O)	2.25 (3H, s), 3.20 (3H, s), 6.45 (1H, s), 7.00–7.80 (8H, m), 8.90 (2H, s)
8f	52	170–172	$C_{27}H_{21}N_3O_3$ (methanol)	3250 (NH), 3080 (CH arom.), 2895 (CH aliph.), 1680 (C=O)	2.25 (3H, s), 3.20 (3H, s), 6.40 (1H, s), 7.00–7.80 (13H, m), 8.90 (1H, s)
9a	60	280–282	$C_{20}H_{16}N_4O$ (ethanol)	3250–3200 (NH), 3060 (CH arom.), 2890 (CH aliph.), 1700 (C=O)	2.28 (3H, s), 6.40 (1H, s), 7.00–7.80 (9H, m), 8.80 (3H, s)
9b	55	290–292	$C_{26}H_{20}N_4O$ (methanol)	3200–3180 (NH), 3050 (CH arom.), 2880 (CH aliph.), 1690 (C=O)	2.25 (3H, s), 6.40 (1H, s), 7.00–7.80 (14H, m), 8.90 (2H, s)

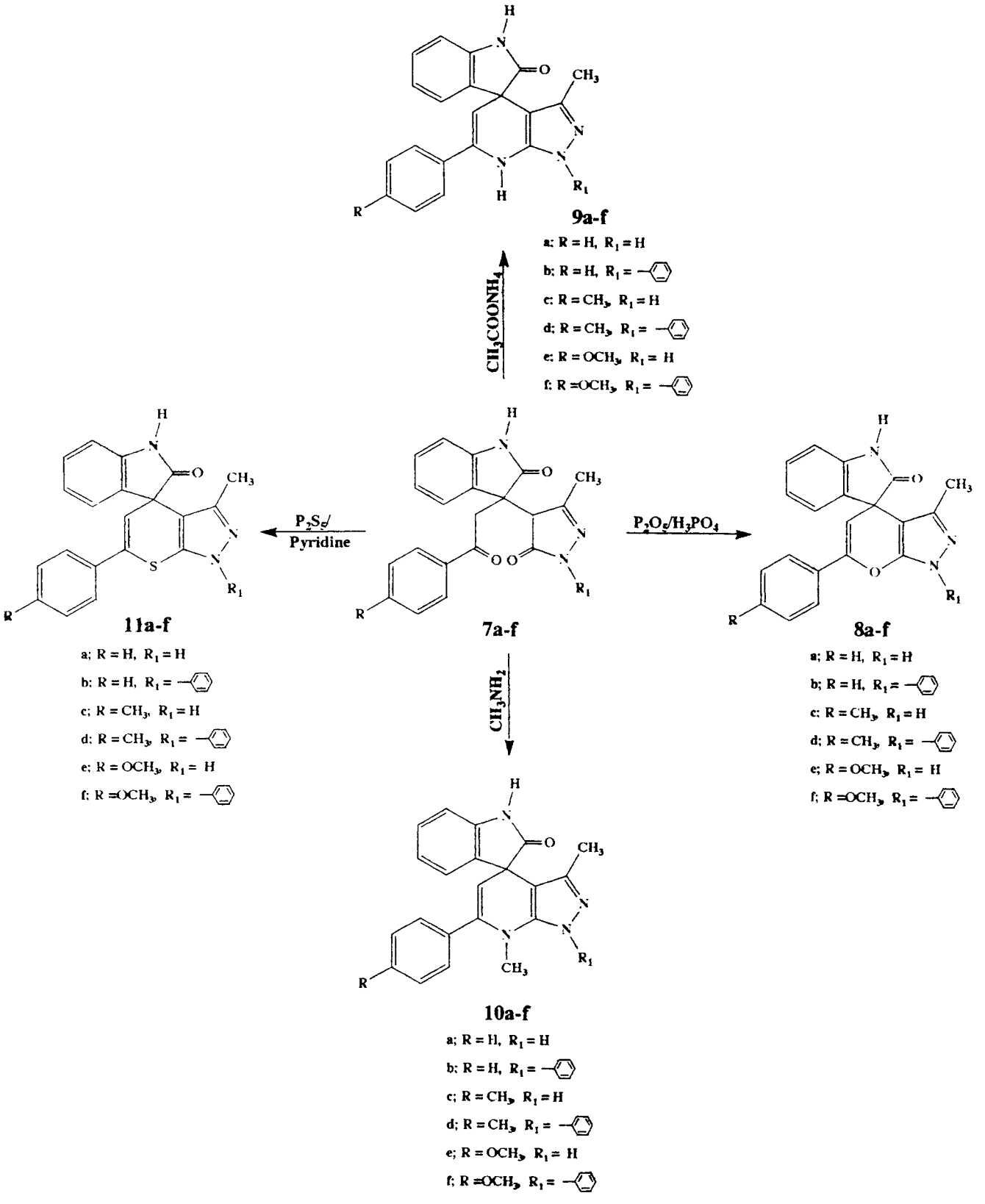
ring, 7.00–7.70 (9H, m) for the aromatic protons, and 8.80 (2H, s) for NH protons of the pyrazoline and indole rings. Reactions of compounds **7a–f** with phosphorus pentaoxide/phosphoric acid afforded 3′-methyl-6′-arylspiro[indoline-3,4′-(pyrazolo[4,5b]pyran]-2-one derivatives **8a–f** in good yields (Scheme 2). The structures of compounds **8a–f** were confirmed on the basis of their elemental analyses and spectroscopic data (Table 1). The ^1H NMR spectrum of **8a** (CF_3COOH) showed the following signals: δ 2.28 (3H, s) for the protons of the methyl group of the pyrazoline ring at $C_{3'}$, 6.40 (1H, s) for the proton at $C_{5'}$ in the pyran moiety, 7.00–7.80 (9H, m) for the aromatic protons, and 8.80 (2H, s) for the protons of the NH groups of the pyrazoline and indoline rings. Reaction of compounds **7a–f** with ammonium acetate yielded 3′-methyl-6′-arylspiro[indoline-3,4′-(pyrazolo[4,5-b]dihydropyridine)]-2-one derivatives **9a–f** in good yields (Scheme 2). The structure assignments of compounds **9a–f** were based on their elemental and spectral analyses (Table 1). The IR spectrum of **9a** showed characteristic absorption bands at 3250–3200 cm^{-1} corresponding to the stretching vibrations of NH groups of pyrazoline, dihydropyridine, and indoline rings, 3060 cm^{-1} for the aromatic carbon–hydrogen stretching, 2890

TABLE 1 Continued Physical Data of 3-Phenacyl-3-[4′-(3′-methylpyrazolin-5′-onyl)]indoline-2-ones **7a–f** and Spiro[indoline-3-pyrazoloheterocycles]-2-one derivatives **8a–f**, **9a–f**, **10a–f**, and **11a–f**

Compound No.	Yield (%)	MP (°C)	Molecular Formula[a] (solvent of Crystallization)	IR (KBr), cm^{-1}	^1H NMR (CF_3COOH), δ(TMS)
9c	58	220–222	$C_{21}H_{18}N_4O$ (ethanol)	3250 (NH), 3050 (CH arom.), 2900 (CH aliph.), 1690 (C=O)	2.25 (3H, s), 2.30 (3H, s), 6.40 (1H, s), 7.00–7.80 (8H, m), 8.90 (3H, s)
9d	57	260–262	$C_{27}H_{22}N_4O$ (methanol)	3250 (NH), 3050 (CH arom.), 2950 (CH aliph.), 1685 (C=O)	2.25 (3H, s), 2.30 (3H, s), 6.40 (1H, s), 7.00–7.80 (13H, m), 8.90 (2H, s)
9e	56	320–322	$C_{21}H_{18}N_4O_2$ (ethanol)	3200 (NH), 3050 (CH arom.), 2900 (CH aliph.), 1685 (C=O)	2.25 (3H, s), 3.20 (3H, s), 6.40 (1H, s), 7.00–7.80 (8H, m), 8.90 (3H, s)
9f	54	330–332	$C_{27}H_{22}N_4O_2$ (methanol)	3250 (NH), 3050 (CH arom.), 2900 (CH aliph.), 1680 (C=O)	2.25 (3H, s), 3.20 (3H, s), 6.40 (1H, s), 7.00–7.80 (13H, m), 8.90 (2H, s)
10a	65	270–272	$C_{21}H_{18}N_4O$ (ethanol-water) 4 : 1	3250 (NH), 3050 (CH arom.), 2900 (CH aliph.), 1690 (C=O)	2.25 (3H, s), 3.16 (3H, s), 6.35 (1H, s), 7.00–7.80 (9H, m), 8.90 (2H, s)
10b	61	310–312	$C_{27}H_{22}N_4O$ (ethanol-water) 4 : 1	3200 (NH), 3050 (CH arom.), 2900 (CH aliph.), 1690 (C=O)	2.28 (3H, s), 3.16 (3H, s), 6.35 (1H, s), 7.00–7.80 (14H, m), 8.90 (2H, s)
10c	60	340–342	$C_{22}H_{20}N_4O$ (ethanol-water) 3 : 2	3200 (NH), 3050 (CH arom.), 2900 (CH aliph.), 1680 (C=O)	2.25 (3H, s), 3.15 (3H, s), 6.40 (1H, s), 7.00–7.80 (8H, m), 8.90 (2H, s)
10d	60	270–272	$C_{28}H_{24}N_4O$ (ethanol-water) 3 : 1	3250 (NH), 3060 (CH arom.), 2890 (CH aliph.), 1685 (C=O)	2.28 (3H, s), 3.16 (3H, s), 6.30 (1H, s), 7.00–7.80 (13H, m), 8.90 (1H, s)
10e	57	>350	$C_{22}H_{20}N_4O_2$ (ethanol-water) 1 : 1	3250–3200 (NH), 3060 (CH arom.), 2890 (CH aliph.), 1690 (C=O)	2.26 (3H, s), 3.15 (3H, s), 3.20 (3H, s), 6.35 (1H, s), 7.00–7.80 (8H, m), 8.90 (2H, s)
10f	55	320–322	$C_{28}H_{24}N_4O_2$ (ethanol-water) 1 : 1	3200 (NH), 3050 (CH arom.), 2890 (CH aliph.), 1690 (C=O)	2.25 (3H, s), 3.15 (3H, s), 3.20 (3H, s), 6.35 (1H, s), 7.00–7.80 (13H, m), 8.90 (1H, s)
11a	60	190–192	$C_{20}H_{15}N_3OS$ (acetone-water) 1 : 1	3220 (NH), 3060 (CH arom.), 2900 (CH aliph.), 1690 (C=O)	2.28 (3H, s), 6.40 (1H, s), 7.00–7.80 (9H, m), 8.80 (2H, s)
11b	60	180–182	$C_{26}H_{19}N_3OS$ (acetone-water) 1 : 1	3240 (NH), 3060 (CH arom.), 2900 (CH aliph.), 1690 (C=O)	2.25 (3H, s), 6.40 (1H, s), 7.00–7.80 (14H, m), 8.80 (1H, s)
11c	58	250–252	$C_{21}H_{17}N_3OS$ (acetone-water) 1 : 1	3200 (NH), 3050 (CH arom.), 2890 (CH aliph.), 1690 (C=O)	2.25 (3H, s), 2.30 (3H, s), 6.35 (1H, s), 7.00–7.90 (9H, m), 8.80 (2H, s)
11d	56	240–242	$C_{27}H_{21}N_3OS$ (acetone-water) 2 : 1	3220 (NH), 3060 (CH arom.), 2900 (CH aliph.), 1690 (C=O)	2.25 (3H, s), 2.30 (3H, s), 6.35 (1H, s), 7.00–7.80 (13H, m), 8.80 (1H, s)
11e	55	220–222	$C_{21}H_{17}N_3O_2S$ (acetone-water) 2 : 1	3220 (NH), 3060 (CH arom.), 2900 (CH aliph.), 1680 (C=O)	2.25 (3H, s), 3.20 (3H, s), 6.30 (1H, s), 7.00–7.80 (8H, m), 8.90 (2H, s)
11f	55	280–282	$C_{27}H_{21}N_3O_2S$ (acetone-water) 2 : 1	3225 (NH), 3050 (CH arom.), 2900 (CH aliph.), 1685 (C=O)	2.25 (3H, s), 3.20 (3H, s), 6.35 (1H, s), 7.00–7.80 (13H, m), 8.80 (1H, s)

[a]All the prepared compounds gave satisfactory elemental analyses.

cm^{-1} for the aliphatic carbon–hydrogen stretching, and 1700 cm^{-1} for the carbonyl group of the indole ring. The ^1H NMR spectrum of **9a** (CF_3COOH) showed the following signals: δ 2.28 (3H, s) for the methyl protons, 6.40 (1H, s) for the proton at $C_{5'}$, 7.00–7.80 (9H, m) for the aromatic protons, and 8.80 (3H, s) for the NH protons of pyrazoline, dihydropyridine, and indoline rings. Also, the reactions of compounds **7a–f** with methanolic methylamine [19] afforded 3′,7′-dimethyl-6′-arylspiro[indoline-3,4′-


9a-f
a: R = H, R1 = H
b: R = H, R1 = —⬡
c: R = CH3, R1 = H
d: R = CH3, R1 = —⬡
e: R = OCH3, R1 = H
f: R = OCH3, R1 = —⬡
CH3COONH4
P2S5/ Pyridine
P2O5/H3PO4
CH3NH2
11a-f
a; R = H, R1 = H
b; R = H, R1 = —⬡
c; R = CH3, R1 = H
d; R = CH3, R1 = —⬡
e; R = OCH3, R1 = H
f; R = OCH3, R1 = —⬡
7a-f
8a-f
a; R = H, R1 = H
b; R = H, R1 = —⬡
c; R = CH3, R1 = H
d; R = CH3, R1 = —⬡
e; R = OCH3, R1 = H
f; R = OCH3, R1 = —⬡
10a-f
a; R = H, R1 = H
b; R = H, R1 = —⬡
c; R = CH3, R1 = H
d; R = CH3, R1 = —⬡
e; R = OCH3, R1 = H
f; R = OCH3, R1 = —⬡

SCHEME 2

(pyrazolo[4,5-b]dihydropyridine)]-2-one derivatives **10a–f** in good yields (Scheme 2). Compounds **10a–f** were identified by conventional methods, such as elemental and spectral analyses (IR and ^{1}H NMR spectra) (Table 1). The ^{1}H NMR spectrum of **10a** (CF_3COOH) showed the following signals: δ 2.25 (3H, s) for the methyl protons at $C_{3'}$, 3.16 (3H, s) for the methyl protons of the N–CH_3 group, 6.35 (1H, s) for the proton at $C_{5'}$, 7.00–7.80 (9H, m) for the aromatic protons, and 8.90 (2H, s) for NH protons of pyrazoline and indoline rings. Reactions of compounds **7a–f** with phosphorus pentaoxide in pyridine afforded 3′-methyl-6′-arylspiro[indoline-3,4′-(pyrazolo[4,5-b]thiopyran)]-2-one derivatives **11a–f** in good yields (Scheme 2). The structures of compounds **11a–f** were established from their elemental analyses and spectroscopic data (Table 1). The IR spectrum of **11a** showed characteristic strong absorption bands at 3220 cm^{-1} corresponding to the stretching vibration of the NH group of the pyrazoline and indoline rings, 3060 cm^{-1} for the aromatic carbon–hydrogen stretching, 2900 cm^{-1} for the aliphatic carbon–hydrogen, 1690 cm^{-1} for the carbonyl group at C_2 of the indoline ring, and 730 cm^{-1} for C–S bond stretching. The ^{1}H NMR spectrum of **11a** (CF_3COOH) showed the following signals: δ 2.28 (3H, s) for the methyl group protons at $C_{3'}$, 6.40 (1H, s) for the proton at $C_{5'}$, 7.00–7.80 (9H, m) for the aromatic protons, and 8.80 (2H, s) for the protons of the NH groups of pyrazoline and indoline rings.

EXPERIMENTAL

The time required for completion of each reaction was monitored by thin-layer chromatography (TLC). Melting points are uncorrected. ^{1}H NMR spectra were measured on an EM-360 90 MHz spectrophotometer. IR spectra were recorded on a Pye-Unicam SP 200 G spectrophotometer. Elemental analyses were determined by use of a Perkin-Elmer 240 C microanalyzer.

Preparation of 1-[3-(2-Oxoindolinylidine)]acetic acid (3)

This compound was prepared according to our reported method [36].

1-[3-(2-Oxoindolinylidine)]acetyl chloride (4) *and 3-(2-Oxoindolinylidine)]acetophenone Derivatives* (5a–c)

These compounds were prepared according to the reported method [36].

Preparation of 3-Aracyl-3-[4′-(3′-methylpyrazolin-5′-onyl)]indoline-2-one Derivatives (7a–f)

General Procedure. Each compound **5a–c** (0.001 mol) was dissolved in 25 mL of pyridine. To this solution, 3-methyl-1H-pyrazolin-5-one **6a** and/or 3-methyl-1-phenylpyrazolin-5-one **6b** (0.001 mol) was added portionwise. The reaction mixture was refluxed for 12 hours, then the solvent was removed by distillation and the residue was poured into 25 mL of cold 10% hydrochloric acid, whereby the crude product precipitated. It was filtered off and crystallized from the proper solvent (Table 1).

3-Phenacyl-3-[4′-(3′-methyl-1H-pyrazolin-5′-onyl)]indoline-2-one Derivatives (7a)

A 0.249 g (0.001 mol) amount of **5a** was treated with 0.098 g (0.001 mol) of **6a** in 25 mL of pyridine, according to the previous general procedure, to yield 0.208 g (60% yield) of **7a**, mp 340–342°C, IR (KBr): 3200–3100 (NH), 3050 (CH arom.), 2950 (CH aliph.), 1680 and 1710 (C=O); ^{1}H NMR (CF_3COOH): δ 2.25 (3H, s), 4.50 (2H, s), 5.80 (1H, s), 7.00–7.70 (9H, m), 8.80 (2H, s).

Synthesis of Spiro[indoline-3-pyrazoloheterocycles]-2-one Derivatives 8a–f, 9a–f, 10a–f *and* 11a–f

General Procedure. Each compound **7a–f** (0.001 mol) was treated with the calculated amount of phosphorus pentoxide in phosphoric acid at 120°C for 1/2 hour, or ammonium acetate at 140°C for 6 hours, or with methanolic methylamine at reflux temperature for 8 hours, or with phosphorus pentasulfide in pyridine at reflux temperature for 8 hours, then the reaction mixture was cooled to room temperature, and poured into 25 mL of cold water, whereby the target product precipitated. It was filtered off and crystallized from the proper solvent (Table 1).

3′-Methyl-6′-phenylspiro[indoline-3,4′-(pyrazolo[4,5-b]pyran)]-2-one (8a)

A 0.35 g (0.001 mol) amount of **7a** was treated with 0.5 g of phosphorus pentoxide in 5 mL of phosphoric acid, and the reaction mixture was heated at 120°C for 1/2 hour, then treated according to the previous general procedure to yield 0.2 g (61% yield) of **8a**, mp 155–157°C, IR (KBr): 3200 (NH), 3060 (CH arom.), 2890 (CH aliph.), 1705 (C=O). ^{1}H NMR (CF_3COOH): δ 2.28 (3H, s), 6.40 (1H, s), 7.00–7.80 (9H, m), 8.80 (2H, s).

3′-Methyl-6′-phenylspiro[indoline-3,4′-(pyrazolo[4,5-b]dihydropyridin)]-2-one (9a)

A 0.35 g (0.001 mol) amount of **7a** was treated with 0.7 g of ammonium acetate and then fused at 140°C for 6 hours according to the previous general procedure to give 0.2 g (60% yield) of **9a**, mp 280–282°C, IR (KBr): 3250–3200 (NH), 3060 (CH arom.), 2890 (CH aliph.), 1700 (C=O). ^{1}H NMR (CF_3COOH): δ

2.28 (3H, s), 6.40 (1H, s), 7.00–7.80 (9H, m), 8.80 (3H, s).

3,7'-Dimethyl-6'-phenylspiro[indoline-3,4'-(pyrazolo[4,5-b]dihydropyridin)]-2-one (10a)

A 0.35 g (0.001 mol) amount of **7a** was treated with 5 mL of methanolic methylamine (40%) and then refluxed for 8 hours according to the described general procedure to afford 0.22 g (65% yield) of **10a**, mp 270–272°C, IR (KBr): 3250 (NH), 3050 (CH arom.), 2900 (CH aliph.), 1690 (C=O). ^{1}H NMR (CF_3COOH): δ 2.25 (3H, s), 3.16 (3H, s), 6.35 (1H, s), 7.00–7.80 (9H, m), 8.90 (2H, s).

3'-Methyl-6'-phenylspiro[indoline-3,4'-(pyrazolo[4,5-b]thiopyran)]-2-one (11a)

A 0.35 g (0.001 mol) amount of **7a** reacted with 0.25 g (0.001 mol) of phosphorus pentasulfide in 10 mL of pyridine according to the previous general procedure to give 0.2 g (60% yield) of **11a**, mp 190–192°C, IR (KBr): 3220 (NH), 3060(CH arom.), 2900 (CH aliph.), 1690 (C=O), 730 (C–S). ^{1}H NMR (CF_3COOH): δ 2.28 (3H, s), 6.40 (1H, s), 7.00–7.80 (9H, m), 8.90 (2H, s).

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