Syntheses of Some 3-[1′(1′*H*)-Substituent-pyrazol-5′-yl]benzo[5,6]coumarins

EL-DEEN, Ibrahim Mohey[*,a] **AL-WAKEEL, El-Sayed Ismail**[a,b] **El-MAWLA, Ahmed Gad**[a,b]

[a] *Faculty of Education, Suez Canal University, Port-said, Egypt*

[b] *Faculty of Science, Suez Canal University, Ismailia, Egypt*

3-[1′(1′*H*)-Substituent-pyrazol-5′-yl]benzo[5,6]coumarins and 3-(1′,2′-oxazol-5′-yl)benzo[5,6]coumarin were prepared via condensation of 3-(2′-formyl-1′-chlorovinyl) benzo[5,6] coumarin with hydrazine derivatives or hydroxylamine. Reaction of 3-[1′(1′*H*)-pyrazol-5′-yl]benzo[5,6]coumarin with alkyl halides, olefinic compounds or acid chlorides are described.

Keywords heterocycle synthesis, pyrazol-5′-ylbenzo[5,6] coumarin, alkylation at pyrazole nitrogen.

Considerable interest has been shown in coumarinyl-heterocycles on account of their pharmacological activity.[1-3] According to our previous work,[4] 3-acetylbenzo[5,6]coumarin (**1**) reacted with $POCl_3$-DMF affording 3-(2′-formyl-1′-chlorovinyl) benzo[5,6] coumarin (**2**). As an extension of our previous work,[4-11] the present work describes the syntheses of some heterocyclic compounds containing benzocoumarin and pyrazole moieties using **2** as a key starting material. The reactions studied and the products obtained are depicted in Schemes 1 and 2.

Treatment of compound **2** with hydrazine bisulphate, phenylhydrazine sulphate and hydroxylamine hydrochloride in the presence of fused sodium acetate in dimethyl formamide solution under reflux, gave 3-[1′(1′*H*)-substituent-pyrazol-5′-yl]benzo[5,6]coumarins (**3**) and 3-(1′,2′-oxazol-5′-yl)benzo[5,6]coumarin (**4**), respectively.

Alkylation of 3-[1′(1′*H*)-pyrazol-5′-yl]benzo[5,6] coumarin (**3a**) with an alkyl halide (namely, benzyl bromide, benzoylmethyl bromide or ethyl chloroacetate) in the presence of fused sodium acetate in DMF led to the formation of 3-[1′(1′H)-alkylpyrazol-5′-yl]benzo[5,6] coumarins (**5a—c**).

Condensation of compound **5b** with an aromatic aldehyde (such as benzaldehyde or 4-chlorobenzaldehyde) in the presence of piperidine by fusion at 120 ℃ afforded the corresponding 3-[1′(1′H)-(2″-aryl-1″-aroylvinyl) pyrazol-5′-yl]benzo[5,6]coumarins (**6a, 6b**). And also, the condensation of compound **5c** with hydrazine hydrate in boiling ethanol afforded the corresponding 3-[1′(1′*H*)-(hydrazinocarbonylmethyl)pyrazol-5′-yl]benzo[5,6]coumarin (**7**).

In the present work the reaction of compound **3a** with dimethyl sulphate at room temperature in aqueous sodium hydroxide solution gave the corresponding 3-[1′(1′*H*)-methylpyrazol-5′-yl]benzo[5,6]coumarin (**8**).

In a detailed work,[12] the reaction of compound **3a** with an olefinic compound (namely, acrylonitrile or methyl acrylate) in the presence of potassium carbonate under Michael reaction conditions afforded the corresponding 3-[1′(1′*H*)-alkylpyrazol-5′-yl]benzo[5,6] coumarins (**9a, 9b**).

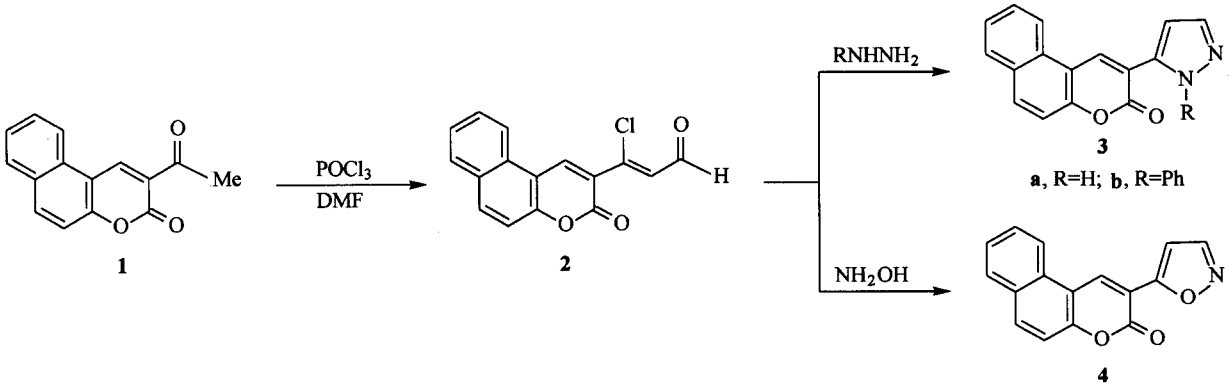
3-[1′-(Tetrazol-5″-yl-ethyl) pyrazol-5′-yl]benzo[5,6]coumarin (**10**) was prepared previously[13] by the reaction of compound **9a** with sodium azide in the presence of ammonium chloride in distilled DMF.

Treatment of compound **9b** with hydrazine hydrate in boiling ethanol led to the formation of 3-[1′(1′*H*)-hydrazinocarbonylethyl) pyrazol-5′-yl]-benzo[5,6]coumarin (**11**). On the other hand, the acylation or benzoylation of compound **3a** with an acid chloride (such as acetyl chlo-

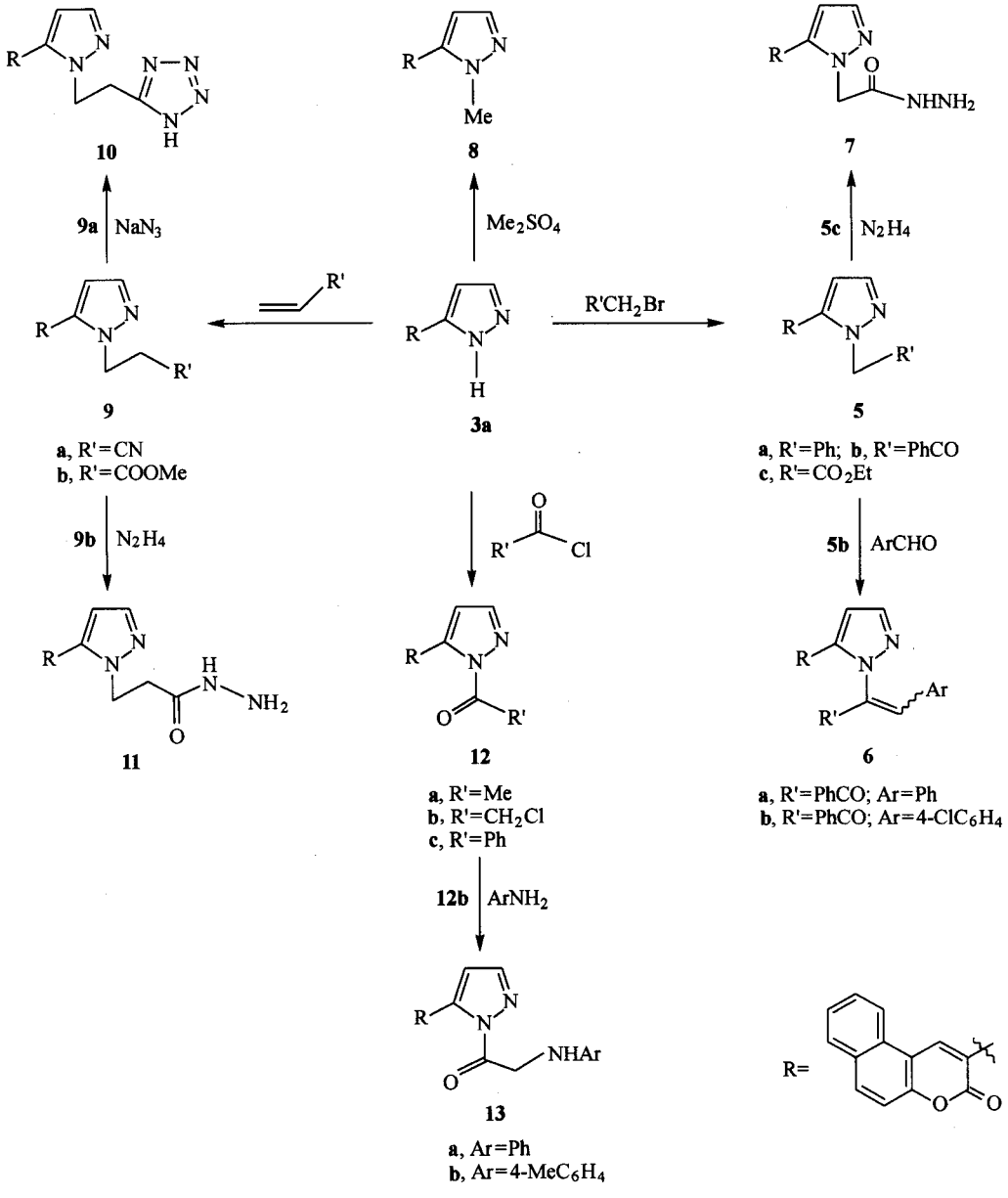
* E-mail: eldeen@yahoo.com

Received July 31, 2001; revised and accepted December 3, 2001.

Scheme 1



Scheme 2



ride, chloroacetyl chloride or benzoyl chloride) in acetic acid afforded the corresponding 3-[1′(1′*H*)-(alkylcarbonyl)pyrazol-5′-yl]benzo[5,6]coumarins (**12a—c**).

Treatment of compound **12b** with a primary amine (namely, aniline or *p*-toluidine) in ethanol solution gave the corresponding 3-[1′(1′*H*)-(arylaminoacetyl)-pyrazol-5′-yl]benzo[5,6]coumarins (**13a, 13b**).

Experimental

Melting points were determined on a Kofler hot-stage apparatus and were uncorrected. IR spectra were obtained using a Perkin-Elmer 297 spectrophotometer as Nujol mulls. ^{1}H NMR spectra were recorded on a Bruker Model AW 80 (80 MHz) spectrometer with tetramethylsilane as the internal standard. Mass spectra were recorded on a VG-250 spectrometer with ionization energy maintained at 70 eV. Microanalyses were performed on a Perkin-Elmer 2408 CHN analyzer.

3-(2′-Formyl-1′-chlorovinyl)benzo[5,6]coumarin (**2**)

3-(2′-Formyl-1′-chlorovinyl) benzo[5, 6] coumarin (**2**) was prepared according to the literature procedure.[4] The crude product was recrystallized from ethanol to give **2** as yellow crystal, yield 85%, m.p. 95—96 ℃; ^{1}H NMR ($CDCl_3$, 80 MHz) δ: 7.15—8.20 (m, 8H, ArH and olefinic proton), 10.23 (d, J = 1.2 Hz, 1H, -CHO); IR (KBr) ν_{max}: 3082, 1721, 1668, 1614, 790 cm^{-1}; MS (70 eV) *m/z* (%): 284 (M^+, 98), 221 (100), 142 (63). Anal. calcd for $C_{16}H_9ClO_3$: C 67.49, H 3.16, Cl 12.48; found C 67.03, H 2.97, Cl 12.01.

3-[1′(1′H)-Substituent-pyrazol-5′-yl]benzo[5,6]coumarins (**3a, 3b** *and* **4**)

To a solution of **2** (0.01 mol) in DMF (50 mL) was added a solution of a hydrazine derivative (namely, hydrazine bisulphate or phenylhydrzaine sulphate) or hydroxylamine hydrochloride (0.01 mol) in water (5 mL) dropwise. Then fused sodium acetate (0.02 mol) was added and the reaction mixture was heated under reflux for 6 h. The reaction mixture was cooled and poured into water. The resulting product was filtered, washed with water, dried and recrystallized from ethanol to give **3** or **4**.

3-[1′(1′H)-Prazol-5′-yl]benzo[5,6]coumarin (**3a**) Yellow crystal, yield 86%, m.p. 282 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 6.31 (d, J = 1.4 Hz, 1H, H-4 of pyrazole), 7.20—8.14 (m, 8H, ArH and H-3 of pyrzaole), 10.61 (s, 1H, NH); IR (KBr) ν_{max}: 3230, 1723, 1625, 1610, 1096 cm^{-1}; MS (70 eV) *m/z* (%): 262 (M^+, 82), 261 (M^+ - 1, 23), 205 (75), 144 (79), 105 (77). Anal. calcd for $C_{16}H_{10}N_2O_2$: C 73.28, H 3.82, N 10.69; found C 73.02, H 3.53, N 10.31.

3-[1′(1′H)-Phenylpyrazol-5′-yl]benzo[5,6]coumarin (**3b**) Grey crystal, yield 68%, m.p. 179 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 6.33 (d, J = 1.41 Hz, 1H, H-4 of pyrazole), 7.01—8.20 (m, 13H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 3081, 1722, 1628, 1612, 1099 cm^{-1}; MS (70 eV) *m/z* (%): 339 (M^+ + 1, 78), 338 (M^+, 35), 248 (43); 1631 (25). Anal. calcd for $C_{22}H_{14}N_2O_2$: C 78.10, H 4.14, N 8.28; found C 77.87, H 3.95, N 8.01.

3-(1′,2′-Oxazol-5′-yl)benzo[5,6]coumarin (**4**) Brown crystal, yield 86%, m.p. 152 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 6.35 (d, J = 1.2 Hz, 1H, H-4 of oxazole), 7.21—8.19 (m, 8H, ArH and H-3 of oxazole); IR (KBr) ν_{max}: 3081, 1719, 1667, 1615, 1021 cm^{-1}; MS (70 eV) *m/z* (%): 263 (M^+, 52), 223 (79), 63 (42). Anal. calcd for $C_{16}H_9NO_3$: C 73.00, H 3.42, N 5.32; found C 72.82, H 3.10, N 5.03.

3-[1′(1′H)-Alkylpyrazol-5′-yl]benzo[5,6]coumarins (**5a—c**)

A mixture of **3a** (0.01 mol), an alkyl halide (namely, benzyl bromide, benzoyl-methyl bromide or ethyl chloroacetate) (0.01 mol) and fused sodium acetate (0.03 mol) in DMF (60 mL) was heated under reflux for 8 h. The reaction mixture was cooled and poured into water. The resulting product was filtered, washed with water, dried and recrystallized from ethanol to give **5**.

3-[1′(1′H)-Phenymethylpyrazol-5′-yl]benzo[5,6]coumarin (**5a**) Yellow crystal, yield 66%, m.p. 105 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 2.51 (s, 2H, CH_2), 6.32 (d, J = 1.4 Hz, 1H, H-4 of pyrazole), 7.09—8.21 (m, 13H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 3096, 2989, 1722, 1624, 1610, 1097 cm^{-1}; MS (70 eV) *m/z* (%): 352 (M^+, 12),

256 (11), 207 (21), 149 (30), 73 (100). Anal. calcd for $C_{23}H_{16}N_2O_2$: C 78.41, H 4.55; N 7.95; found C 78.12; H 4.29; N 7.62.

3-[1′(1′*H*)-*Benzoylmethylpyrazol-5′-yl*]*benzo*[5,6]*coumarin* (**5b**) Grey crystal, yield 78%, m.p. 175 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 3.10 (s, 2H, CH_2), 6.31 (d, J = 1.4 Hz, 1H, H-4 of pyrazole), 7.03—8.22 (m, 13H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 3100, 2969, 1718, 1630, 1614, 1160, 1101 cm^{-1}; MS (70 eV) *m/z* (%): 380 (M^+, 45), 324 (3), 245 (45), 183 (100), 157 (55), 76 (58). Anal. calcd for $C_{24}H_{16}N_2O_3$: C 75.79, H 4.21, N 7.37; found C 75.43, H 3.99, N 7.02.

3-[1′(1′*H*)-*Ethoxycarbonylmethylpyrazol-5′-yl*]*benzo*[5,6]*coumarin* (**5c**) Brown crystal, yield 63%, m.p. 138 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 1.23 (t, J = 1.8 Hz, 3H, CH_3), 3.01 (s, 2H, CH_2CO), 4.01 (q, J = 1.6 Hz, 2H, OCH_2), 6.30 (d, J = 1.4 Hz, 1H, H-4 of pyrazole), 7.20—8.19 (m, 8H, ArH and H-3of pyrazole); IR (KBr) ν_{max}: 3100, 2969, 1746, 1719, 1630, 1614, 1160, 1101 cm^{-1}. Anal. calcd for $C_{20}H_{16}N_2O_4$: C 68.97, H 4.60, N 8.05; found C 68.63, H 4.28, N 7.86.

3-[1′(1′*H*)-(2″-*Aryl*-1″-*arylvinyl*)*pyrazol*-5′-*yl*]*benzo*[5,6]*coumarins* (**6a**, **6b**)

A mixture of **5b** (0.01 mol), an aromatic aldehyde (such as benzaldehyde or 4-chlorobenzaldehyde) (0.01 mol) and piperidine (1 mL) was fused on an oil-bath at 120 ℃ for 1 h. The reaction mixture was added to DMF (60 mL) and heated under reflux for 4 h. The reaction mixture was cooled and poured onto ice-HCl. The solid formed was filtered off, washed with water, dried and recrystallized from ethanol to give **6**.

3-[1′(1′*H*)-(2″-*Phenyl*-1″-*benzoylvinyl*)*pyrazol*-5′-*yl*]*benzo*[5,6]*coumarin* (**6a**) Yellow crystal, yield 60%, m.p. 193 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 6.30 (d, J = 1.4Hz, 1H, H-4 of pyrazole), 6.71 (s, 1H, CH olefinic), 7.02—8.23 (m, 18H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 3099, 1719, 1658, 1625, 1613, 1091 cm^{-1}. Anal. calcd for $C_{31}H_{20}N_2O_3$: C 79.49, H 4.27, N 5.98; found C 79.30, H 4.15, N 5.73.

3-[1′(1′*H*)-(2″-(*p*-*Chlorophenyl*)-1″-*benzoylvinyl*)*pyrazol*-5′-*yl*]*benzo*[5,6]-*coumarin* (**6b**) Yellow crystal, yield 61%, m.p. 183 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 6.31 (d, J = 1.4 Hz, 1H, H-4 of pyrazole), 6.72 (s, 1H, CH olefinic), 7.12—8.22 (m, 17H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 3092, 1718, 1657, 1621, 1612, 1091, 798 cm^{-1}. Anal. calcd for $C_{31}H_{19}ClN_2O_3$: C 74.03, H 3.78, N 5.57, Cl 7.06; found: C 73.92, H 3.66, N 5.32, Cl 6.87.

3-[1′(1′*H*)-(*Hydrazinocarbonylmethyl*)*pyrazol*-5′-*yl*]*benzo*[5,6]*coumarin* (**7**)

A solution of **5c** (0.01 mol) and hydrazine hydrate (0.02 mol) in ethanol (50 mL) was heated under reflux for 6 h, then cooled and acidified with diluted hydrochloric acid (2%). The crude product obtained was filtered, washed with water, dried and recrystallized from acetic acid to give **7** as brown crystal, yield 73%, m.p. 245 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 3.12 (s, 2H, CH_2CO), 6.31 (d, J = 1.4 Hz, 1H, H-4 of pyrazole), 7.21—8.20 (m, 8H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 3336, 3251, 3175, 1721, 1685, 1625, 1612, 1098 cm^{-1}. Anal. calcd for $C_{18}H_{14}N_4O_3$: C 64.67, H 4.19, N 16.77; found C 64.32; H 3.97; N 16.46.

3-[1′(1′*H*)-*Methylpyrazol*-5′-*yl*]*benzo*[5,6]*coumarin* (**8**)

To a solution of **3a** (0.01 mol) and sodium hydroxide (20 mL, 1 mol/L) was added dimethylsulpahte (0.01 mol). The reaction mixture was stirred at room temperature for 2 h. The solid formed was filtered off and recrystallized from dimethyl formamide to give **8** as brown crystal, yield 81%, m.p. 298 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 3.11 (s, 3H, NCH_3), 6.31 (d, J = 1.4 Hz, 1H, H-4 of pyrazole), 7.20—8.19 (m, 8H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 2969, 1722, 1623, 1612, 1098 cm^{-1}; MS (70 eV) *m/z* (%): 276 (M^+, 98), 261 (32), 183 (55), 91 (21), 51 (25). Anal. calcd for $C_{17}H_{12}N_2O_2$: C 73.91, H 4.35, N 10.14; found C 73.78, H 4.22, N 10.01.

3-[1′(1′*H*)-*Alkylpyrazol*-5′-*yl*]*benzo*[5,6]*coumarins* (**9a**, **9b**)[12]

A mixture of **3a** (0.01 mol), an olefinic comp-

ound (namely, acrylonitrile or methyl acrylate) (0.01 mol) and potassium carbonate (0.03 mol) in dimethyl formamide (60 mL) was heated under reflux for 6 h. The reaction mixture was cooled and poured onto water. The resulting product was filtered, washed with water, dried and recrystallized from ethanol to give **9**.

3-[1′(1′*H*)-*Cyanoethylpyrazol-5′-yl*]*benzo*[5,6]*coumarin* (**9a**) Grey crystal, yield 78%, m.p. 88 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 2.29(t, J = 1.8 Hz, 2H, CH_2CN), 2.51 (t, J = 1.8 Hz, 2H, NCH_2), 6.31 (d, J = 1.4 Hz, 1H, H-4 of pyrazole), 7.21—8.23 (m, 8H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 3059, 2989, 2230, 1725, 1615, 1010 cm^{-1}. MS (70 eV) *m/z* (%): 316 (M^+ + 1, 82), 315 (M^+, 35), 262 (86), 205 (51), 135 (81), 63 (54). Anal. calcd for $C_{19}H_{13}N_3O_2$: C 72.38, H 4.12, N 13.33; found C 72.03, H 4.09, N 13.03.

3-[1′(1′*H*)-*Methoxycarbonylethylpyrazol-5′-yl*]*benzo*[5,6]*coumarin* (**9b**) Grey crystal, yield 66%, m.p. 190 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 2.21 (t, J = 1.8 Hz, 2H, CH_2CO), 2.52 (t, J = 1.8 Hz, 2H, NCH_2), 2.68 (s, 3H, OCH_3), 6.31 (d, J = 1.4 Hz, 1H, H-4 of pyrazole), 7.20—8.21 (m, 8H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 2965, 1735, 1721, 1627, 1612, 1102, 1098 cm^{-1}; MS (70 eV) *m/z* (%): 348 (M^+, 35), 316 (27), 288 (85), 262 (76), 135 (36), 63 (51). Anal. calcd for $C_{20}H_{16}N_2O_4$: C 68.96, H 4.59, N 8.05; found C 68.55, H 4.23, N 7.89.

3-[1′(1′*H*)-(2″-*Tetrazol-5″-yl-ethyl*)*pyrazol-5′-yl*]*benzo*[5,6]*coumarin* (**10**)[13]

A mixture of **9a** (0.01 mol), sodium azide (0.023 mol) and ammonium chloride (0.03 mol) in distilled dimethyl formamide (70 mL) was heated under reflux for 16 h, then cooled and poured onto water. The resulting solid was filtered, washed with water, dried and recrystallized from acetic acid to give **10** as light brown crystal, yield 71%, m.p. 210—211 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 3.13 (t, J = 1.8 Hz, 2H, CH_2), 2.53 (t, J = 1.8 Hz, 2H, NCH_2), 6.30 (d, J = 1.4 Hz, 1H, H-4 of pyrazole), 7.19—8.21 (m, 8H, ArH and H-3 of pyrazole), 10.21 (s, 1H, NH); IR (KBr) ν_{max}: 3360, 3059, 2986, 1723, 1625, 1010 cm^{-1}; MS (70 eV) *m/z* (%): 359 (M^+ + 1, 23), 358 (M^+, 31), 262 (89), 96 (75), 76 (51). Anal. calcd for $C_{19}H_{14}N_6O_2$: C 63.69, H 3.91, N 23.46; found C 63.37, H 3.65, N 23.14.

3-[1′(1′*H*)-2′-(*Hydrazinocarbonylethyl*)*pyrazol-5′-yl*]*benzo*[5,6]*coumarin* (**11**)

A solution of **9b** (0.01 mol), hydrazine hydrate (0.02 mol) in ethanol (50 mL) was heated under reflux for 6 h, then cooled and acidified with diluted hydrochloric acid (2%). The crude product washed with water, dried and recrystallized from ethanol to give **11** as brown crystal, yield 81%, m.p. 140—191℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 2.23 (t, J = 1.8 Hz, 2H, CH_2CO), 2.35 (t, J = 1.8 Hz, 2H, NCH_2), 6.32 (d, J = 1.4 Hz, 1H, H-4 of pyrazole), 7.21—8.19 (m, 8H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 3378, 3251, 3172, 1723, 1665, 1622, 1618, 1090 cm^{-1}. Anal. calcd for $C_{19}H_{16}N_4O_3$: C 65.52, H 4.60, N 16.09; found C 65.25, H 4.31, N 15.87.

3-[1′(1′*H*)-(*Alkylcarbonyl*)*pyrazol-5′-yl*]*benzo*[5,6]-*coumarins* (**12a—c**)

A mixture of **3a** (0.01 mol) and an acid chloride (such as acetyl chloride, chloracetyl chloride or benzoyl chloride) (0.01 mol) in acetic acid (60 mL) was heated under reflux for 4 h. The solid formed after cooling was filtered off, dried and recrystallized from acetic acid to give **12**.

3-[1′(1′*H*)-*Acetylpyrazol-5′-yl*]*benzo*[5,6]*coumarin* (**12a**) Brown crystal, yield 82%, m.p. 223 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 2.10 (s, 3H, CH_3), 6.31 (d, J = 1.4 Hz, 1H, H-4 of pyrazole), 7.21—8.19 (m, 8H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 3081, 2975, 1723, 1675, 1627, 1613, 1020 cm^{-1}; MS (70 eV) *m/z* (%): 304 (M^+, 37), 262 (27), 225 (75), 139 (87), 63 (74); Anal. calcd for $C_{18}H_{12}N_2O_3$: C 71.05, H 3.95, N 9.21; found C, 70.82, H 3.63, N 9.01.

3-[1′(1′*H*)-*Chloroacetylpyrazol-5′-yl*]*benzo*[5,6]*coumarin* (**12b**) Yellow crystal, yield 66%, m.p. 325 ℃; ^{1}H NMR (DMSO-d_6, 80 MHz) δ: 3.66 (s, 2H, CH_2Cl), 6.30(d, J = 1.4 Hz, 1H, H-4 of pyrazole), 7.20—8.21 (m, 8H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 3073, 2961, 1721, 2687, 1625, 1613,

1020, 780 cm^{-1}; MS (70 eV) *m/z* (%): 341 (M^+ + 2, 3), 339 (M^+, 10), 302 (52), 286 (20), 262 (5), 245 (7), 229 (7), 153 (15), 137 (20), 83 (25). Anal. calcd for $C_{18}H_{11}ClN_2O_3$: C 63.82, H 3.25, N 8.27, Cl 10.48; found C 63.47, H 3.02, N 8.20, Cl 10.10.

3-[1′(1′*H*)-*Benzoylpyrazol-5′-yl*] *benzo*[5,6] *coumarin* (**12c**) Yellow crystal, yield 77%, m.p. 183 ℃; ^1H NMR (DMSO-d_6, 80 MHz) δ: 6.32 (d, *J* = 1.4 Hz, 1H, H-4 of pyrazole), 7.18—8.19 (m, 13H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 3082, 1725, 1672, 1623, 1615, 1023 cm^{-1}; MS (70 eV) *m/z* (%): 367 (M^+ + 1, 3), 366 (M^+, 10), 262 (13), 236 (30), 196 (15), 149 (100), 105 (35), 97 (27), 57 (61). Anal. calcd for $C_{23}H_{14}N_2O_3$: C 75.41, H 3.83, N 7.65; found C 75.16, H 3.48, N 7.33.

3-[1′(1′*H*)-(*Arylaminoacetyl*) *pyrazol-5′-yl*] *benzo*[5,6] *coumarins* (**13a**,**13b**)

A solution of **12b** (0.01 mol) and a primary amine (namely, aniline or *p*-toludine) (0.01 mol) in ethanol (70 mL) was heated under reflux for 4 h. The solid formed after cooling was filtered off, dried and recrystallized from ethanol to give **13**.

3-[1′(1′*H*)-(*Phenylaminoacetyl*) *pyrazol-5′-yl*] *benzo*[5,6] *coumarin* (**13a**) Brown crystal, yield 60%, m.p. 190 ℃; ^1H NMR (DMSO-d_6, 80 MHz) δ: 2.83 (s, 2H, CH_2), 4.31 (s, 1H, NH), 6.31 (d, *J* = 1.4 Hz, 1H, H-4 of pyrazole), 7.20—8.21 (m, 13H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 3336, 3073, 2961, 1723, 1625, 1623, 1612, 1023 cm^{-1}; MS (70 eV) *m/z* (%): 395 (M^+, 25), 394 (M^+-1, 81), 337 (13), 218 (12), 170 (25), 77 (100). Anal. calcd for $C_{24}H_{17}N_3O_3$: C 72.91, H 4.30, N 10.63; found C 72.62, H 4.02, N 10.37.

3-[1′(1′*H*)-(*p-Methylphenylaminoacetyl*) *pyrazol-5′-yl*] *benzo*[5,6] *coumarin* (**13b**) Brown crystal, yield 52%, m.p. 181 ℃; ^1H NMR (DMSO-d_6, 80 MHz) δ: 2.1 (s, 3H, CH_3), 2.81 (s, 2H, CH_2), 4.32 (s, 1H, NH), 6.30 (d, *J* = 1.4 Hz, 1H, H-4 of pyrazole), 7.19—8.20 (m, 12H, ArH and H-3 of pyrazole); IR (KBr) ν_{max}: 3335, 3071, 2959, 1720, 1652, 1627, 1618, 1028 cm^{-1}. Anal. calcd for $C_{25}H_{19}N_3O_3$: C 73.35, H 4.64, N 10.26; found C 73.21, H 4.43, N 10.12.

References

1 Faragy, A. E.; Yassin, F.; Abdel-Ghani, E.; El-Said, N.; Saleh, R. *Heterocycles* **1992**, *34*, 25 [*Chem. Abstr.* **1992**, *116*, 214426f].

2 Nicolaides, D. N.; Fylaktakidou, K. C.; Litinas, K. E. *J. Heterocycl. Chem.* **1996**, *33*, 967 [*Chem. Abstr.* **1996**, *125*, 221731r].

3 Eltamany, S. H.; El-Deen, I. M.; Abd El-Fattah, M. E. *Pak. J. Sci. Ind. Res.* **1995**, *38*, 115 [*Chem. Abstr.* **1996**, *125*, 300909h].

4 El-Deen, I. M. *Chin. J. Chem.* **1998**, *16*, 528[*Chem. Abstr.* **1999**, *130*, 223147g].

5 El-Deen, I. M. *Chin. J. Chem.* **1998**, *16*, *533*[*Chem. Abstr.* **1999**, *130*, 223197y].

6 El-Deen, I. M. *Chin. J. Chem.* **1999**, *17*, 391 [*Chem. Abstr.* **1999**, *131*, 228703r].

7 El-Deen, I. M. *J. Serb. Chem. Soc.* **1998**, *63*, 367 [*Chem. Abstr.* **1998**, *129*, 81701m].

8 El-Deen, I. M. *J. Indian Chem. Soc.* **1992**, *69*, 601 [*Chem. Abstr.* **1993**, *119*, 95435h].

9 El-Deen, I. M.; Ibrahim, H. K. *Phosphorus, Sulfur Silicon Relat. Elem.* **2000**, *160*, 241.

10 El-Deen, I. M.; Ibrahim, H. K.; Mahmoud, F. F. *Chin. J. Chem.* **2000**, *18*, 590.

11 El-Deen, I. M.; Abd El-Fattah, M. E. *Indian J. Heterocycl. Chem.* **1999**, *8*, 319 [*Chem. Abstr.* **1999**, *131*, 170327c].

12 Saleh, R. M. *Indian J. Chem.* **1991**, *30*, 313 [*Chem. Abstr.* **1991**, *114*, 22839p].

13 Raman, R.; Parmar, S. S.; Singh, S. P. *J. Heterocycl. Chem.* **1980**, *17*, 137.

(E0107314FZ DONG, L. J.)