Tricyclic Heterocyclic Systems: Pyrazolo[5′,4′:4,5]- and pyrazolo-[3′,4′:4,5]pyrano[2,3-*b*]pyridine Derivatives

Fabrizio Melani, Lucia Cecchi*, Vittoria Colotta,
Giovanna Palazzino and Guido Filacchioni

Dipartimento di Scienze Farmaceutiche, Universita' di Firenze,
Via Gino Capponi, 9, 50121 Firenze, Italy

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By reacting 2-chloronicotinoyl chloride with acetyl or benzoyl acetate, ethyl 2-methyl- or 2-phenyl-4-oxopyrano[2,3-*b*]pyridine-3-carboxylates were prepared. The nucleophilic rearrangement of the latter with hydrazines gave rise to the title compounds.

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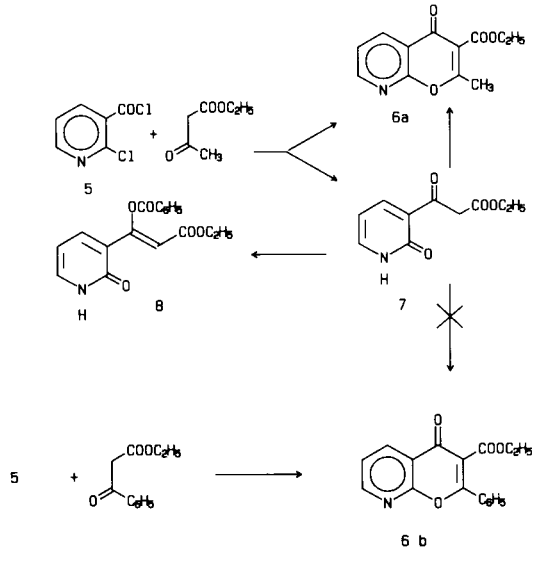
Little attention has been paid in the literature to pyrazolopyranopyridine fused ring systems; there are only a few examples of linear systems [1-3] and only one of an angular system [4]. Following our previous researches on tricyclic heterocyclic systems [5-11] interacting with the benzodiazepine receptor we hereby report the synthesis of some derivatives of pyrazolo[5′,4′:4,5]pyrano[2,3-*b*]pyridines **1a-b**, **2** and pyrazolo[3′,4′:4,5]pyrano[2,3-*b*]pyridines **3-4**. Allowing 2-chloronicotinoyl chloride (**5**) to react with ethyl acetoacetate or benzoylacetate, ethyl 2-methyl- or 2-phenyl-4-oxopyrano[2,3-*b*]pyridine-3-carboxylates **6a-b** were obtained. From the reaction of **5** with ethyl acetoacetate, a mixture of **6a** and ethyl 3-(2-oxopyridin-3-yl)-3-oxopropanoate (**7**) was isolated. The latter reacted with acetyl chloride to yield compound **6a**, while from the reaction of **7** with benzoyl chloride the benzoyloxy derivative **8** was isolated (see Scheme 1).

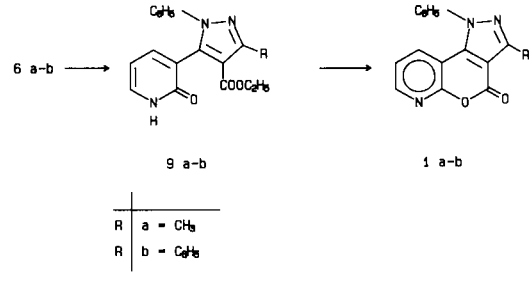
Scheme 1



From the reaction of the ethyl 3-azachromonecarboxylate derivatives **6a-b** with phenylhydrazine the nucleophilic rearrangement took place, leading to ethyl 1,3-disubstituted 5-(2-oxopyridin-3-yl)pyrazole-4-carboxylates **9a-b** (see Scheme 2). The nucleophilic rearrangement of **6a** with hydrazine gave rise to the tautomeric pyrazole-4-carboxylate **10** (see Scheme 3). The structures of **9a-b** are in agreement with the fact that in phenylhydrazine only the β-nitrogen has the necessary nucleophilicity to carry out the attack on the 2-electrophilic position of azachromones **6a-b**. By heating **9a-b**, **10** at their melting points the tricyclic derivatives **1a-b**, **4** were easily obtained.

Allowing **6b** to react with methylhydrazine, in agreement with the latter's twofold nucleophilic reactivity, a mixture of the two isomers ethyl 1-methyl-3-phenyl-5-(2-oxopyridin-3-yl)pyrazole-4-carboxylate (**11**) and ethyl 1-methyl-3-(2-oxopyridin-3-yl)-5-phenylpyrazole-4-carboxylate (**12**) was isolated. This mixture was never separated, compounds **11-12** being seen in the ^{1}H nmr spectrum of the mixture.

Scheme 2



Scheme 3

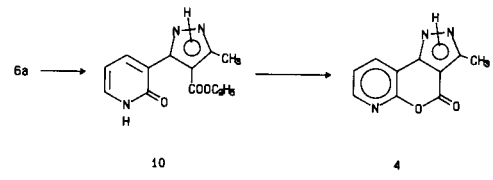
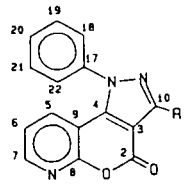
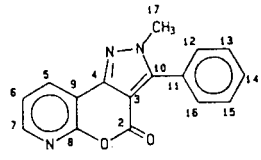
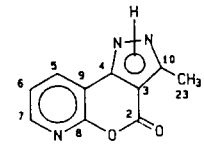


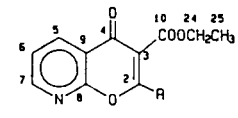
Table 1

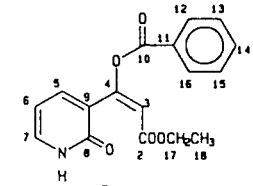
^{13}C Chemical Shift Assignments (ppm)

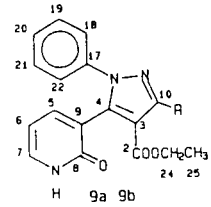


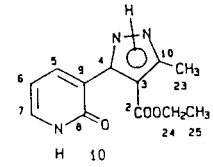


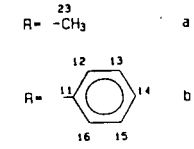












Product No.	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
1a	156.33	107.09 [a]	140.40	131.50	120.02	149.73	160.21	107.48 [a]	150.82
1b	155.75	105.63 [a]	141.60	131.61	120.06	150.07	158.11	107.12 [a]	152.63
3	156.16	105.25 [a]	147.01	131.70	120.56	148.97	158.33	110.42 [a]	146.59
4	157.85	109.79	145.61 [b]	131.83	120.98	148.66	157.00	104.08	145.61 [b]
6a	167.28	117.91 [a]	174.42	136.51	122.28	153.18	159.64	118.27 [a]	164.10
6b	163.48	117.90 [a]	175.25	136.56	122.44	153.60	159.98	118.46 [a]	164.27
8	163.34	108.36	152.75	140.04	105.53	138.19	159.91	120.63	164.25
9a	162.81	112.26	142.40	142.68	104.51	136.76	160.53	121.74	150.36
9b	163.19	112.92	141.52	143.37	106.20	135.98	162.89	121.95	153.50
10	163.60	109.61	145.90 [b]	139.99	104.55	135.54	161.06	123.96	145.90 [b]

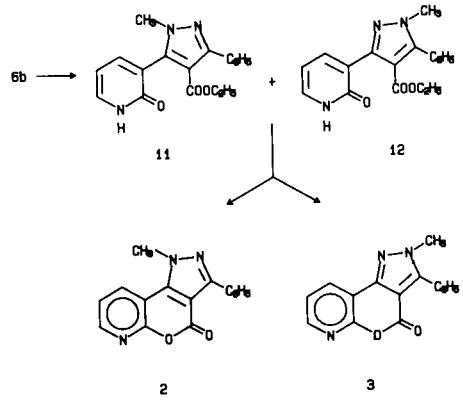
Product No.	C-11	C-12	C-13	C-14	C-15	C-16	C-17	C-18	C-19
1a							138.84	129.94	126.48
1b	132.68	129.00	128.27	130.63	128.27	129.00	138.95	130.12	126.76
3	126.39	129.81	128.53	130.15	128.53	129.81	38.18		
4									
6a									
6b	331.18	128.59	128.11	131.78	128.11	128.59			
8	128.85	130.00 [a]	128.85 [a]	133.94	128.85 [a]	130.00 [a]	59.67	13.91	
9a							139.14	128.89	124.56
9b	132.51	129.32	127.64	128.07 [a]	127.64	129.32	139.23	128.82	124.82
10									

Product No.	C-20	C-21	C-22	C-23	C-24	C-25
1a	130.31	126.48	129.94	12.62		
1b	129.51	126.76	130.12			
3						
4				10.82		
6a				19.28	61.64	13.30
6b					61.86	13.60
8						
9a	128.00	124.56	128.89	13.74	59.25	13.82
9b	128.26 [a]	124.82	128.82		59.95	13.65
10				12.05	59.01	12.05

[a] The assignment may be reversed. [b] Broad signals.

The crude mixture was fused and chromatographed to give, as its main product, 2-methyl-3-phenyl-2*H*-pyrazolo-[3′,4′:4,5]pyrano[2,3-*b*]pyridin-4-one (**3**) as well as a small amount of 1-methyl-3-phenyl-1*H*-pyrazolo[5′,4′:4,5]pyrano-[2,3-*b*]pyridin-4-one (**2**) (see Scheme 4).

Scheme 4



In conclusion, the reactivity of azachromones **6a-b** towards hydrazine, methylhydrazine and phenylhydrazine gave rise to different products depending on the different nucleophilicity of the hydrazines. The same reactivity is reported [12] for chromones towards hydrazines.

The structures of pyrazole derivatives **9a-b**, **10** and those of the tricyclic compounds **1a-b**, **2-4** were confirmed by ^1H and ^{13}C nmr data. The chemical shifts and coupling constants of the synthesized compounds are listed in Tables 1 and 2. An arbitrary numbering is used to identify all carbon atoms. The assignment is in agreement with those previously reported [7-9, 13].

EXPERIMENTAL

Silica gel plates (Merck F_{254}) and silica gel 60H (Merck) were used for analytical and column chromatography respectively. Reagent quality solvents were used without further purification. Melting points were determined on a Büchi 510 capillary melting point apparatus and are uncorrected. Microanalyses were performed with a Perkin-Elmer 260 elemental analyzer. Mass spectra were obtained using a Perkin-Elmer 270 mass

Table 2

J_{CH} Coupling Constants (Hz)

Product No.	C-2	C-3	C-4	C-5	C-6	C-7	C-10
1a			$^3J_{4H5}$ 4.7	$^1J_{5H5}$ 167.1	$^1J_{6H6}$ 168.3	$^1J_{7H7}$ 183.7	$^2J_{10H23}$ 6.7
				$^2J_{5H6}$ 1.4	$^2J_{6H5}$ <.5	$^2J_{7H6}$ 3.8	
				$^3J_{5H7}$ 7.1	$^2J_{6H7}$ 8.5	$^3J_{7H5}$ 8.1	
3			$^3J_{4H5}$ 4.2	$^1J_{5H5}$ 165.1		$^1J_{7H7}$ 182.4	
4				$^1J_{5H5}$ 168.0	$^1J_{6H6}$ 169.9	$^1J_{7H7}$ 183.2	
				$^2J_{5H6}$ <.5	$^2J_{6H5}$ 2.8	$^2J_{7H7}$ 3.3	
				$^3J_{5H7}$ 6.6	$^2J_{6H7}$ 8.5	$^3J_{7H5}$ 8.1	
6a	$^2J_{2H23}$ 6.6		$^3J_{4H5}$ 3.8	$^1J_{5H5}$ 167.1	$^1J_{6H6}$ 168.0	$^1J_{7H7}$ 182.3	
				$^2J_{5H6}$ 4.2	$^2J_{6H5}$ 3.3	$^2J_{7H6}$ 4.7	
				$^3J_{5H7}$ 6.6	$^3J_{6H7}$ 8.2	$^3J_{7H5}$ 8.5	
6b	$^3J_{2H12}$ 3.8		$^3J_{4H5}$ 3.8	$^1J_{5H5}$ 162.3		$^1J_{7H7}$ 182.5	
	$^3J_{2H16}$ 3.8			$^2J_{5H6}$ 3.3		$^2J_{7H6}$ 4.7	
				$^3J_{5H7}$ 6.4		$^3J_{7H5}$ 8.1	
9a		$^3J_{3H23}$ 2.4	$^3J_{4H5}$ 5.0	$^1J_{5H5}$ 162.8	$^1J_{6H6}$ 170.9	$^1J_{7H7}$ 180.4	$^2J_{10H23}$ 6.6
				$^2J_{5H6}$ 2.6	$^2J_{6H5}$ 1.1	$^2J_{7H6}$ 5.7	
				$^3J_{5H7}$ 8.5	$^2J_{6H7}$ 3.8	$^3J_{7H5}$ 7.7	
9b			$^3J_{4H5}$ 4.9	$^1J_{5H5}$ 161.3	$^1J_{6H6}$ 171.4		$^3J_{10H12}$ 3.8
				$^2J_{5H6}$ 1.6	$^2J_{6H5}$ 6.2		$^3J_{10H18}$ 3.8
				$^3J_{5H7}$ 8.5	$^2J_{6H7}$ 3.8		
10				$^1J_{5H5}$ 161.4	$^1J_{6H6}$ 169.5	$^1J_{7H7}$ 179.4	
				$^2J_{5H6}$ 1.9	$^2J_{6H5}$ 1.9	$^2J_{7H6}$ 7.1	
				$^3J_{5H7}$ 8.5	$^2J_{6H7}$ 4.3	$^3J_{7H5}$ 8.5	

spectrometer and samples were introduced by direct inlet probe (DIE); operating conditions: ions accelerating voltage 2.5 kV, electron energy 70 eV and ions source temperature 160°. The ir spectra were recorded with a Perkin-Elmer 1420 spectrometer in nujol mulls. The ^1H nmr spectra were obtained with a Varian EM 360L instrument using tetramethylsilane (TMS) as internal standard. The natural abundance ^{13}C nmr spectra were run on a Varian FT-80A spectrometer at 20 MHz in the Fourier transform mode. All samples were recorded in 10 mm o.d. tubes at the probe temperature (30°) with a concentration in chloroform-d or dimethyl sulfoxide-d_6 of approximately 10% w/v which provided the deuterium signal for the field frequency lock. Chemical shifts were measured relatively to the central peak of the solvent (deuteriochloroform = 76.9 ppm, DMSO-d_6 = 39.6 ppm) and corrected to internal TMS. Typical acquisition parameters include: a spectral width of 5000 Hz, a flip angle of 42° and an interpulse delay between acquisition of 510 μsec. Chemical shift values were reproducible to better than ± 0.05 ppm. The decoupled spectra were obtained without pulse delay. The coupled spectra with nuclear Overhauser effect (nOe) were obtained by putting the decoupler on for a pulse delay of 1.6 seconds and off for an acquisition time of 0.8 seconds. The coupling constants are reported in Hz.

2-Chloronicotinoyl Chloride (**5**).

To a suspension of 2-chloronicotinic acid (5 g, 31.7 mmoles) in anhydrous benzene (50 ml), thionyl chloride (6.9 ml, 95.3 mmoles) was added. The mixture was refluxed for 2 hours. The solvent and the excess of thionyl chloride were distilled off at reduced pressure. The oily residue was dried under nitrogen, washed with ligroin to give a crystalline solid, yield 4.7 g (84%), mp 56-59° (Lit [14], mp 55-58°); ir: 1790 (COCl) cm^{-1}; ^1H nmr (deuteriochloroform): 7.50 (dd, 1 H, H-5), 8.45 (dd, 1 H, H-4), 8.64 ppm (dd, 1 H, H-6).

Ethyl 2-methyl-4-oxo-4*H*-pyrano[2,3-*b*]pyridine-3-carboxylate (**6a**).

Method A.

To a stirred suspension of sodium (0.25 g, 11 mmoles) in anhydrous diethyl ether (150 ml), ethyl acetoacetate (1.39 ml, 11 mmoles) was added. When all the sodium was dissolved a solution of 2-chloronicotinoyl chloride (**5**, 1.94 g, 11 mmoles) in diethyl ether (150 ml) was then added dropwise. The reaction was carried out at room temperature for 13 days. The suspension was filtered and the solvent evaporated at reduced pressure. The residue was taken up with cyclohexane/ethyl acetate, 1:1, filtered and chromatographed on a silica gel column under pressure, eluting system cyclohexane/ethyl acetate, 1:1. Compound **6a** was contained in the first eluates, yield 0.64 g (25%).

Method B.

To a stirred solution of ethyl 3-(2-oxopyridin-3-yl)-3-oxopropanoate (**7**, 0.5 g, 2.4 mmoles) in anhydrous benzene (25 ml) triethylamine (0.38 ml, 2.7 mmoles) and acetyl chloride (0.21 ml, 3 mmoles) were added. The mixture was stirred at room temperature for 24 hours and then refluxed for 2 hours. The filtered clear solution was evaporated at reduced pressure and the residue chromatographed on a silica gel column under pressure, eluting system benzene/ethyl acetate, 7:3. Compound **6a** was contained in the first eluates, yield 0.1 g, (18%), mp 56-58° (diethyl ether); ms: m/e = 233 (M^+); ir: 1730 ($COOC_2H_5$), 1650 (CO) cm^{-1}; ^1H nmr (deuteriochloroform) 1.40 (t, 3 H, J = 7 Hz, CH_3), 2.60 (s, 3 H, CH_3), 4.43 (q, 2 H, J = 7 Hz, CH_2), 7.3-7.6 (m, 1 H, H-6), 8.5-8.8 ppm (m, 2 H, H-5 + H-7).

Anal. Calcd. for $C_{12}H_{11}NO_4$ (233.2): C, 61.80; H, 4.75; N, 6.01. Found: C, 61.78; H, 4.78; N, 6.06.

Ethyl 2-phenyl-4-oxo-4*H*-pyrano[2,3-*b*]pyridine-3-carboxylate (**6b**).

The title compound was prepared by reacting **5** (1.94 g, 11 mmoles) with 90% ethyl benzoylacetate (2.1 ml, 11 mmoles) as described in the preparation of **6a** (Method A). Purification of **6b** was carried out under the same conditions, yield 1.3 g (40%), mp 128-130° (diethyl ether); ms: m/e = 295 (M^+); ir: 1730 ($COOC_2H_5$), 1640 (CO) cm^{-1}; ^1H nmr (DMSO-d_6): 1.15 (t, 3 H, J = 7 Hz, CH_3), 4.25 (q, 2 H, J = 7 Hz, CH_2), 7.3-8.9 ppm (m, 8 H, 5 H_{arom} + 3 H_{pyrid}).

Anal. Calcd. for $C_{17}H_{13}NO_4$ (295.3): C, 69.15; H, 4.44; N, 4.74. Found: C, 69.35; H, 4.40; N, 4.71.

Ethyl 3-(2-Oxopyridin-3-yl)-3-oxopropanoate (**7**).

The title compound was obtained from the last eluates of the column chromatography of compound **6a** (Method A), yield 0.23 g, (10%), mp 124-125° (diethyl ether); ir: 1730 ($COOC_2H_5$); 1680 (C=O), 1650 (CONH) cm^{-1}; ^1H nmr (deuteriochloroform): 1.23 (t, 3 H, J = 7 Hz, CH_3), 4.12 (s, 2 H, CH_2), 4.20 (q, 2 H, J = 7 Hz, CH_2), 6.50 (m, 1 H, H-5), 7.70 (m, 1 H, H-6), 8.37 (m, 1 H, H-4), 13.3 ppm (s, 1 H, NH).

Anal. Calcd. for $C_{10}H_{11}NO_4$ (209.2): C, 57.41; H, 5.30; N, 6.70. Found: C, 57.68; H, 5.33; N, 6.30.

Ethyl 3-(2-Oxopyridin-3-yl)-3-benzoyloxyacrilate (**8**).

To a stirred solution of **7** (1 g, 4.8 mmoles) in anhydrous benzene (50 ml) triethylamine (0.66 ml, 4.8 mmoles) and benzoyl chloride (0.58 ml, 5 mmoles) were added. The mixture was stirred at room temperature for 24 hours and the filtered clear solution was evaporated at reduced pressure. The resulting residue was washed with ethanol; yield 0.54 g (36%); mp 179-181° (ethanol); ir: 1740, 1710 (CO esters), 1645 (CONH) cm^{-1}; ^1H nmr (DMSO-d_6): 1.07 (t, 3 H, J = 7 Hz, CH_3), 4.02 (q, 2 H, J = 7 Hz, CH_2), 6.38 (m, 1 H, H-5), 7.4-7.9 (m, 6 H, 5 H_{arom} + H-6), 8.0-8.3 (m, 2 H, =CH + H-4), 12.3 ppm (s, 1 H, NH).

Anal. Calcd. for $C_{17}H_{15}NO_5$ (313.3): C, 65.17; H, 4.83; N, 4.47. Found: C, 65.31; H, 5.08; N, 4.61.

Ethyl 1-Phenyl-3-methyl-5-(2-oxopyridin-3-yl)pyrazole-4-carboxylate (**9a**).

To a solution of **6a** (0.23 g, 1 mmoles) in methanol (15 ml) phenylhydrazine (0.1 ml, 1 mmoles) was added. The solution was stirred at room temperature for 18 hours. The solvent was evaporated at reduced pressure and the residue was crystallized; yield 0.21 g (65%), mp 204-205° (ethyl acetate); ms: m/e = 323 (M^+) ir: 1695 ($COOC_2H_5$), 1650 (CONH) cm^{-1}; ^1H nmr (deuteriochloroform): 1.16 (t, 3 H, J = 7 Hz, CH_3), 2.60 (s, 3 H, CH_3), 4.17 (q, 2 H, J = 7 Hz, CH_2), 6.23 (m, 1 H, H-5), 7.2-7.6 (m, 7 H, 5 H_{arom} + 2 H_{pyrid}), 12.5 ppm (s, 1 H, NH).

Anal. Calcd. for $C_{18}H_{17}N_3O_3$ (323.4): C, 66.86, H, 5.30; N, 13.00. Found: C, 66.74; H, 5.02; N, 13.14.

Ethyl 1,3-Diphenyl-5-(2-oxopyridin-3-yl)pyrazole-4-carboxylate (**9b**).

To a solution of **6b** (0.6 g, 2 mmoles) in ethanol (15 ml), phenylhydrazine (0.2 ml, 2 mmoles) was added. The solution was stirred at room temperature for 36 hours. The solvent was evaporated at reduced pressure and the residue was partitioned between ethyl acetate (200 ml) and water (50 ml). The organic layer was dried with sodium sulfate and concentrated at reduced pressure to a residue which was then crystallized, yield 0.54 g (70%), mp 190-193° (ethyl acetate); ms: m/e = 385 (M^+); ir: 1710 ($COOC_2H_5$), 1645 (CONH) cm^{-1}; ^1H nmr (deuteriochloroform): 1.20 (t, 3 H, J = 7 Hz, CH_3), 4.10 (q, 2 H, J = 7 Hz, CH_2), 6.23 (m, 1 H, H-5), 7.2-7.9 (m, 12 H, 10 H_{arom} + 2 H_{pyrid}), 13.1 ppm (s, 1 H, NH).

Anal. Calcd. for $C_{23}H_{19}N_3O_3$ (385.4): C, 71.68; H, 4.97; N, 10.90. Found: C, 71.37; H, 4.90; N, 10.66.

1-Phenyl-3-methyl-1*H*-pyrazolo[5',4':4,5]pyrano[2,3-*b*]pyridine-4-one (**1a**).

Compound **9a** (0.2 g, 0.6 mmole) was heated in an oil bath at 250-280° for 2 hours. The residue was taken up with chloroform/methanol, 8:2 and chromatographed on a silica gel column under pressure, eluting system chloroform/methanol, 8:2; yield 0.08 g (48%), mp 278-279° (ethanol); ms: m/e = 277 (M^+); ir: 1750 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): 2.70 (s, 3 H, CH_3), 6.9-7.7 (m, 7 H, 5 H_{arom} + 2 H_{pyrid}), 8.50 ppm (m, 1 H, H-7).

Anal. Calcd. for $C_{16}H_{11}N_3O_2$ (277.3): C, 69.31; H, 4.00; N, 15.16. Found: C, 69.59; H, 4.16; N, 14.91.

1,3-Diphenyl-1*H*-pyrazolo[5',4':4,5]pyrano[2,3-*b*]pyridine-4-one (**1b**).

The title compound was obtained from **9b** (0.45 g, 1.2 mmoles) as described in the preparation of compound **1a**, yield 0.35 g (86%), mp 299-300° (chloroform); ir: 1745 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): 7.10 (m, 1 H, H-8), 7.4-7.8 (m, 9 H, 8 H_{arom} + H-9), 8.1-8.4 (m, 2 H,

2 H_{arom}), 8.52 ppm (m, 1 H, H-7).

Anal. Calcd. for $C_{21}H_{13}N_3O_2$ (339.4): C, 74.33; H, 3.86; N, 12.38; Found: C, 74.59; H, 4.03; N, 12.13.

Ethyl 3(5)-Methyl-5(3)-(2-oxopyridin-3-yl)pyrazole-4-carboxylate (**10**).

The title compound was obtained by reacting **6a** (1.3 g, 5.6 mmoles) with 98% hydrazine hydrate (0.28 ml, 5.6 mmoles) as described in the synthesis of **9a**, yield 1.2 g (87%), mp 174-176° (ethanol); ms: m/e = 247 (M^+); ir: 1710 ($COOC_2H_5$), 1640 (CONH) cm^{-1}; ^1H nmr (DMSO-d_6): 1.21 (t, 3 H, J = 7 Hz, CH_3), 2.46 (s, 3 H, CH_3), 4.18 (q, 2 H, J = 7 Hz, CH_2), 6.30 (m, 1 H, H-5), 7.39 (m, 1 H, H-6), 7.88 (m, 1 H, H-4), 12.6 ppm (m, 2 H, NH).

Anal. Calcd. for $C_{12}H_{13}N_3O_3$ (247.3): C, 58.29; H, 5.30; N, 16.99. Found: C, 58.40; H, 5.01; N, 17.14.

3-Methyl-1H(2*H*)-pyrazolo[3',4':4,5]pyrano[2,3-*b*]pyridine-4-one (**4**).

The title compound was prepared from **10** (0.2 g, 0.8 mmole) as described in the synthesis of compound **1a**. The residue was taken up with chloroform, collected by suction and recrystallized, yield 0.08 g (50%), mp 224-226° (ethanol); ir: 1750 (C=O) cm^{-1}; ^1H nmr (deuteriochloroform): 2.62 (s, 3 H, CH_3), 7.37 (m, 1 H, H-8), 8.3-8.5 (m, 2 H, H-7 + H-9), 14.0 ppm (s, 1 H, NH).

Anal. Calcd. for $C_{10}H_7N_3O_2$ (201.2): C, 59.70; H, 3.51; N, 20.89. Found: C, 59.48; H, 3.43; N, 20.65.

2-Methyl-3-phenyl-2*H*-pyrazolo[3',4':4,5]pyrano[2,3-*b*]pyridine-4-one (**3**).

To a solution of **6b** (1.3 g, 4.4 mmoles) in methanol (50 ml) methylhydrazine (0.23 ml, 4.4 mmoles) was added. The solution was stirred at room temperature for 18 hours. The solvent was evaporated at reduced pressure to a residue which was crystallized from cyclohexane/ethyl acetate to give a mixture of the two isomer pyrazoles **11** and **12**, yield 0.45 g (32%). The mixture of **11** and **12** was heated in an oil bath at 260° for 1 hour. The residue was taken up with chloroform/methanol, 9:1, and chromatographed on a silica gel column under pressure, eluting system chloroform/methanol, 9:1. The first eluates were discarded; compound **3** was recovered by evaporation of the central eluates, yield 0.15 g (12%), mp 235-236° (ethanol); ^1H nmr (deuteriochloroform): 4.00 (s, 3 H, CH_3), 7.2-7.7 (m, 6 H, 5 H_{arom} + H-8), 8.3-8.6 ppm (m, 2 H, H-7 + H-9).

Anal. Calcd. for $C_{16}H_{11}N_3O_2$ (277.3): C, 69.31; H, 4.00; N, 15.16. Found: C, 69.04; H, 4.21; N, 15.18.

1-Methyl-3-phenyl-1*H*-pyrazolo[5',4':4,5]pyrano[2,3-*b*]pyridine-4-one (**2**).

The title compound was obtained from the last eluates of the column chromatography of compound **3**, yield 0.06 g (5%), mp 295-296° (ethanol); ^1H nmr (deuteriochloroform): 4.41 (s, 3 H, CH_3), 7.3-7.6 (m, 4 H_{arom}), 8.1-8.7 ppm (m, 4 H_{arom}).

Anal. Calcd. for $C_{16}H_{11}N_3O_2$ (277.3): C, 69.31; H, 4.00; N, 15.16. Found: C, 69.18; H, 4.27; N, 14.95.

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