Chemistry of Heterocyclic Compounds, Vol. 42, No. 5, 2006

REACTIONS OF 4-CHLORO-3-FORMYL-COUMARIN WITH PRIMARY AMINES

I. Strakova[1], M. Petrova[1], S. Belyakov[2], and A. Strakovs[1]

The reaction of 4-chloro-3-formylcoumarin with primary amines in the presence of triethylamine was studied. The reaction with aliphatic and aromatic amines leads to N-substituted 4-amino-3-formylcoumarins, whereas hetarylamines react primarily with the formyl group to form a mixture of the Z- and E-isomers of N-substituted 3-aminomethylenechroman-2,4-diones. Replacement of the triethylamine by anhydrous sodium acetate in the reaction of chlorocoumarin with 2-aminopyridines leads to the formation of the condensed benzopyranopyridopyrimidine system as a result of nucleophilic attack of the amino group by the chlorine atom at position 4.

Keywords: N-monosubstituted 4-amino-3-formylcoumarins, 3-aminomethylene-2,4-chromandiones, primary amines, 4-chloro-3-formylcoumarin.

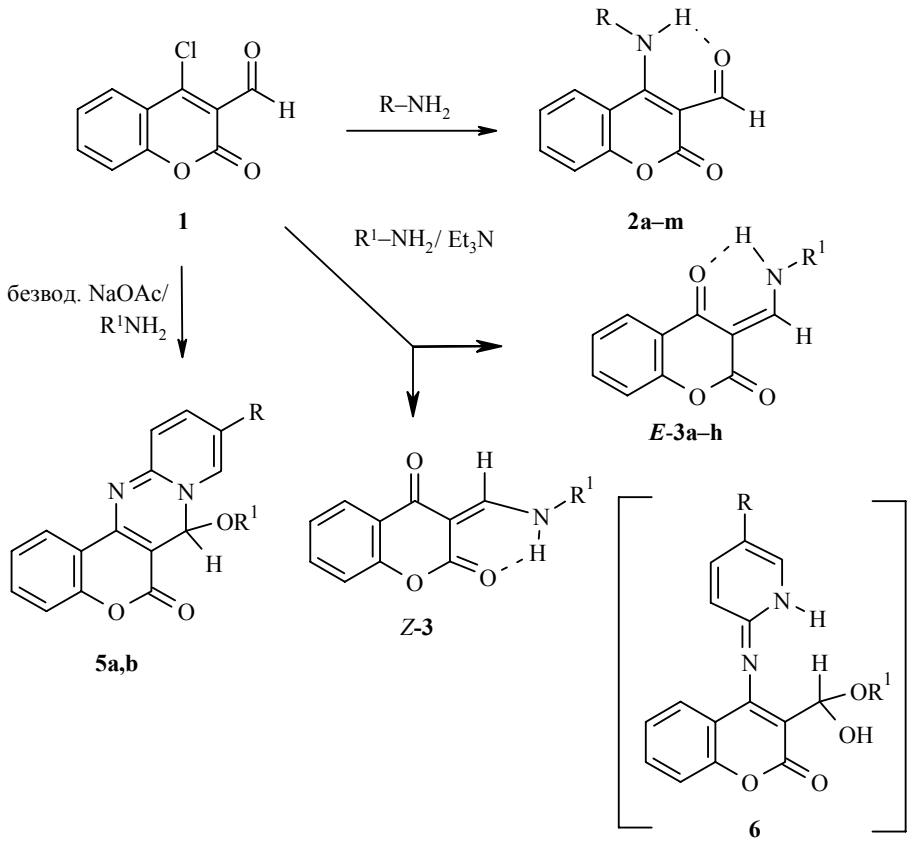
The reaction of 4-chloro-3-formylcoumarin (**1**) with amines has been insufficiently investigated except for some examples of amines [1-5]. Earlier [6] we showed that the reaction of this aldehyde with arylhydrazines can take place initially both at the aldehyde carbonyl and at position 4 with the formation of 1- or 2-substituted 4-oxo[1]benzopyrano[4,3-*c*]pyrazoles respectively.

In the present work we studied the reaction of the coumarin **1** with various primary amines. Here we found that N-monosubstituted 4-amino-3-formylcoumarins **2** are formed in the case of the reaction with aromatic and aliphatic amines and also with 4-aminoantipyrine, whereas the reaction with a series of aminoheterocycles and primarily with 2-aminopyridines takes place at the formyl carbonyl atom with simultaneous hydrolysis of the C–Cl bond at position 4, leading to the substituted 3-aminomethylene-2,4-chromandiones **3**. Only in the reaction with 3-amino-2-chloropyridine did we obtain both isomers **2m** and **3f**.

The composition of the products was confirmed by the data from elemental analysis (Table 1), and their structure was confirmed by the ^{1}H NMR spectra (Table 2) and X-ray crystallographic analysis (Table 3, Figs. 1-3). In the 4-amino-3-formylcoumarins **2** the proton of the N–H group, which forms an intramolecular hydrogen bond with the formyl carbonyl, absorbs in the region of 13.27-11.80 ppm, while the proton of the aldehyde group absorbs in the region of 10.19-9.96 ppm. In the IR spectra the coumarin ester carbonyl of compounds **2** is characterized by an absorption band at 1725-1710 cm^{-1}, while the aldehyde carbonyl, which participates in the formation of a hydrogen bond, gives a band at 1645-1630 cm^{-1}. The structure of the 4-naphth-2-ylamino derivative **2h** was confirmed by the data from X-ray structural investigation. According to the ^{1}H NMR spectra, most of the 3-aminomethylene-2,4-chromandiones **3a**,**b**,**d-g** exist in solution in the form of mixtures of two rotamers *E*-**3** and *Z*-**3**, as indicated by the doublet signals of the two *trans*-located =CH–NH–

[1] Riga Technical University, Riga, Latvia; e-mail: marina@osi.lv. [2] Latvian Institute of Organic Synthesis, Riga, Latvia; e-mail: serg@osi.lv. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 660-668, May, 2006. Original article submitted October 8, 2003; revision submitted September 14, 2005.

fragments of the respective *E*-**3** and *Z*-**3** forms with spin–spin coupling constant ^3J = 13-14 Hz. Only in the ^{1}H NMR spectra of compounds **3c** and **3h** is there one set of signals for the *trans*-located =CH–NH– fragment with ^3J = 13.5 Hz, indicating that the compounds exist in the form of one of the rotamers.



2 a R = 4-$MeOC_6H_4$, **b** R = 4-$MeCOC_6H_4$, **c** R = 3-HO-4-$HO_2CC_6H_3$, **d** R = 2,5-$(EtO_2C)_2C_6H_3$,
e R = 2-$PhSO_2NH$-thiazol-4-yl, **f** R = 4-PhN=NC_6H_4, **g** R=4-Me-coumarin-7-yl,
h R = naphth-4-yl, **i** R=Py-2-CH_2, **j** R = 2-(2-oxoimidazolidin-1-yl)ethyl,
k R = 1-(Ad-1)ethyl, **l** R = 2,3-Me_2-5-oxo-1-Ph-pyrazol-4-yl, **m** R= 2-Cl-Py-3;
3 a R = Py-2, **b** R = 5-Cl-Py-2, **c** R = 3,5-Cl_2-Py-2, **d** R = 3-HO_2C-Py-2, **e** R = 5-CF_3-2-Py-2,
f R = 2-Cl-Py-3, **g** R = pyrimidin-2-yl, **h** R = 3,5-$(EtO_2C)_2$-4-Me-thien-2-yl;
5 a R = R^1 = H, **b** R = Cl, R^1 = Et

It was found that if the triethylamine in the reaction of the coumarin **1** with 2-amino- and 2-amino-5-chloropyridines is replaced by anhydrous sodium acetate the products from initial attack at position 4 are formed in addition to the "normal" compounds **3a** (yield 20%) and **3b** (yield 22%). On account of the presence of the pyridine nitrogen atom (structure **6**) to 7-hydroxy- and 7-ethoxy-6H,7H-[1]benzopyrano[4,3-*d*]pyrimidin-6-ones **5a** and **5b** respectively. The structure was confirmed by the IR and ^{1}H NMR spectra and X-ray crystallographic data.

Figures 1-3 show three-dimensional models of the molecules of **2h**, **5a**, and **5b** with the designations of the atoms and their thermal vibration ellipsoids. Table 3 gives the principal bond lengths in the molecules. In the structure of **2h** there is an intramolecular hydrogen bond N(14)–H···O(13) with length 2.637(3) Å [N–H = 1.01(3), O···H = 1.75(3) Å, N–H···O = 145(2)°], which corresponds to the standard value for intramolecular hydrogen bonds of the NH···O type [7]. An intermolecular hydrogen bond of the OH···N type was

TABLE 1. The Characteristics of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %				mp, °C*	Yield, %
		C	H	N	Cl		
2a	$C_{17}H_{13}NO_4$	69.00 69.14	4.51 4.44	4.62 4.74		164-165	86
2b	$C_{18}H_{13}NO_4$	70.12 70.35	4.30 4.26	4.43 4.56		214-216	97
2c	$C_{17}H_{11}NO_6$	62.71 62.77	3.35 3.41	4.40 4.31		248-250	56
2d	$C_{22}H_{19}NO_7$	64.65 64.54	4.62 4.68	3.49 3.42		197-198	40
2e*[2]	$C_{19}H_{13}N_3O_5S$	53.38 53.49	3.01 3.06	9.92 9.81		237-239	64
2f	$C_{22}H_{13}N_3O_3$	71.71 71.53	3.99 4.09	11.30 11.38		181-182	88
2g	$C_{20}H_{13}NO_5$	68.95 69.16	3.70 3.77	3.94 4.03		subl. >150	71
2h	$C_{20}H_{13}NO_3$	76.01 76.18	4.05 4.15	4.40 4.44		199-200	77
2i	$C_{16}H_{12}N_2O_3$	68.49 68.56	4.27 4.32	10.05 9.99		155-156	54
2j	$C_{15}H_{15}N_3O_4$	59.92 59.79	4.98 5.02	14.03 13.95		258-260	67
2k	$C_{22}H_{25}NO_3$	75.11 75.19	7.21 7.17	4.11 3.99		200-202	43
2l	$C_{21}H_{17}N_2O_4$	67.29 67.19	4.47 4.56	11.29 11.19		240-242	70
2m	$C_{15}H_9ClN_2O_3$	60.05 59.91	3.06 3.02	9.19 9.32	11.60 11.79	262-263	30
3a	$C_{15}H_{10}N_2O_3$	67.83 67.66	3.85 3.79	10.50 10.52		237-240	75
3b	$C_{15}H_{19}ClN_2O_3$	59.71 59.91	3.09 3.02	9.41 9.32		210-215	60
3c	$C_{15}H_8Cl_2N_2O_3$	53.70 53.76	2.45 2.41	8.35 8.36	21.00 21.16	287-289	58
3d	$C_{16}H_{10}N_2O_5$	61.81 61.94	3.33 3.25	8.88 9.03		248-251	71
3e	$C_{16}H_9F_3N_2O_3$	57.30 57.49	2.64 2.72	8.21 8.38		212-213	45
3f	$C_{15}H_9ClN_2O_3$	59.79 59.91	3.03 3.02	9.19 9.32	11.55 11.79	262-263	30
3g	$C_{14}H_9N_3O_3$	62.75 62.92	3.31 3.39	15.61 15.72		230-232	50
3h	$C_{21}H_{19}NO_7S$	58.85 58.73	4.40 4.46	3.15 3.26		166-168	69
5a	$C_{15}H_{10}N_2O_3$	67.54 67.66	3.71 3.79	10.46 10.52		238-242 (dec.)	47
5b	$C_{17}H_{13}ClN_2O_3$	62.19 62.11	4.04 3.99	8.49 8.52	11.00 10.78	204-205 (dec.)	50

* Solvent for crystallization: DMF–H_2O (compounds **2a**,**f**, **3b-d**), DMF–ethanol (compounds **2b**,**e**,**h**,**j**,**l**, **3e**,**g**, **5a**,**b**), ethanol (compounds **2c**,**d**,**i**,**k**,**m**, **3h**), DMF (compounds **2g**, **3a**), DMF–ethanol–water (compound **3f**).

*[2] Found, %: S 14.70. Calculated, %: S 14.97.

found in the crystal structure of **5a**. The length of this bond, equal to 2.846(6) Å [O–H = 0.95(5), N···H = 1.96(5) Å, O–H···N = 153(5)°], is rather larger than the statistical mean of 2.79 Å [8] for H bonds of this type. The packing of the molecules of **5a** in the crystal lattice is shown in Fig. 4.

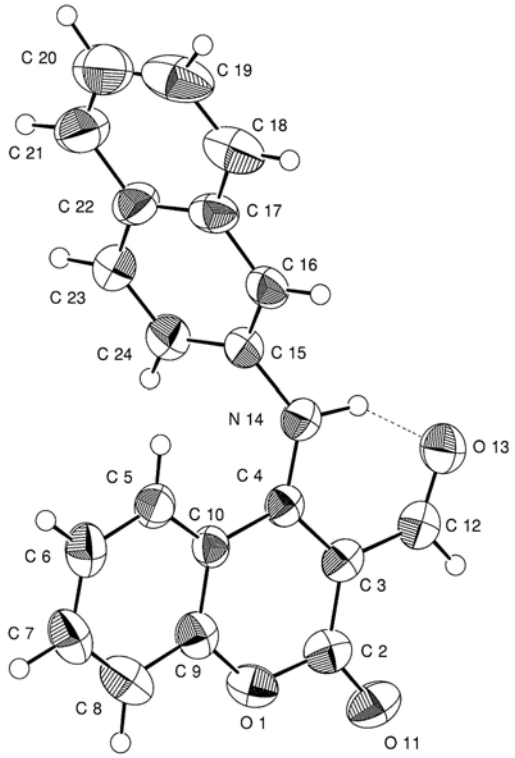


Fig. 1. Three-dimensional model of the **2h** molecule.

TABLE 2. Data from the IR and ^{1}H NMR Spectra of the Synthesized Compounds

Compound	IR spectrum, ν, cm^{-1}		^{1}H NMR spectrum, δ, ppm, (*J*, Hz)*
	CO	NH	
1	2	3	4
2a	1718, 1635	3080	3.79 (3H, s, CH_3); 6.78-7.45 (8H, m, Ar); 10.14 (1H, s, CHO); 13.1 (1H, br. s, NH)
2b	1726, 1682, 1626	3090	2.56 (3H, s, CH_3); 6.86-7.94 (8H, m, Ar); 10.14 (1H, s, CHO); 13.1 (1H, br. s, NH)
2c	1708, 1683, 1622	3150-3050 (NH, OH)	7.05-7.78 (9H, m, Ar, OH, COOH); 10.01 (1H, s, CHO); 12.86 (1H, br. s, NH)
2d	1724, 1714, 1700	3100	3.78 (3H, s, CH_3); 3.81 (3H, s, CH_3); 6.97-8.14 (7H, m, Ar); 10.06 (1H, s, CHO); 13.01 (1H, br. s, NH)
2e	1722, 1630	3140, 3090	6.68-7.81 (11H, m, Ar, NH); 10.02 (1H, s, CHO); 12.53 (1H, br. s, NH)
2f	1725, 1630	3080	7.01-7.96 (13H, m, Ar); 10.04 (1H, s, CHO); 12.69 (1H, br. s, NH)
2g	1737-1727, 1626	3090	2.34 (3H, s, CH_3); 6.58 (1H, s, =CH–); 7.01-7.96 (7H, m, Ar); 10.04 (1H, s, CHO); 12.46 (1H, br. s, NH)
2h	1710, 1638	3070	6.69-7.91 (11H, m, Ar); 10.19 (1H, s, CHO); 13.27 (1H, br. s, NH)
2i	1725, 1635	3090	5.29 (2H, d, *J* = 5, CH_2); 7.29-8.63 (8H, m, Ar); 9.96 (1H, s, CHO); 12.56 (1H, br. s, NH)
2j	1710, 1694, 1630	3330, 3150	3.26 (6H, m, 3CH_2); 4.04 (2H, m, CH_2); 6.46 (1H, br. s, NH); 7.27-8.31 (4H, m, Ar); 9.86 (1H, s, CHO); 11.87 (1H, br. s, NH)
2k	1725, 1631	3080	1.67-2.16 (19H, m, Ad, CH, CH_3); 10.11 (1H, s, CHO); 11.81 (1H, br. s, NH)

TABLE 2 (continued)

1	2	3	4
2l	1726, 1664, 1636	3100	2.22 (3H, s, CH_3); 3.17 (3H, s, CH_3); 6.98-7.87 (9H, m, Ar); 10.17 (1H, s, CHO); 12.56 (1H, br. s, NH)
2m	1720, 1640	3100	6.91-8.42 (7H, m, Ar); 10.17 (1H, s, CHO); 13.11 (1H, br. s, NH)
3a	1692, 1635	3120-3090	7.25-8.44 (8H, m, Ar); 9.28 and 9.51 (1H, dd, *J* = 14, =CH–); 11.78 and 13.10 (1H, two br. d, *J* = 14, NH)
3b	1686, 1648	3210, 3180, 3110	7.33-8.08 (6H, m, Ar); 8.44 (1H, d, *J* = 2.5, Ar); 9.27 and 9.47 (1H, dd, *J* = 14, =CH–); 11.81 and 13.10 (1H, two br. d, *J* = 14, NH)
3c	1722, 1628	3080	7.26-8.26 (4H, m, Ar); 7.76 (1H, d, *J* = 2.5, Ar); 8.31 (1H, d, *J* = 2.5, Ar); 9.26 (1H, d, *J* = 14, =CH–); 4.03 (1H, br. d, *J* = 14, NH)
3d	1718, 1695, 1640	3400, 3100	6.52-8.64 (7H, m, Ar); 9.56 and 9.67 (1H, dd, *J* = 13.5, =CH–); 13.64 and 14.48 (1H, two br. d, *J* = 13.5, NH)
3e	1730, 1632	3230, 3080	7.25-8.22 (6H, m, Ar); 8.83 (1H, br. s, Ar); 9.38 and 9.56 (1H, dd, *J* = 13.5, =CH–); 11.92 and 13.11 (1H, two br. d, *J* = 13.5, NH)
3f	1712, 1634	3080	7.18-8.41 (7H, m, Ar); 9.02 and 9.06 (1H, two d, *J* = 14, =CH–); 12.14 and 13.89 (1H, two br. d, *J* = 14, NH)
3g	1722, 1696, 1640	3080	7.36-8.81 (7H, m, Ar); 9.27 and 9.45 (1H, two d, *J* = 13, =CH–); 11.53 and 12.93 (1H, two br. d, *J* = 13, NH) [7.27-8.61 (7H, m, Ar); 9.48 and 9.61 (1H, two d, *J* = 13.5, =CH–); 11.71 and 13.11 (1H, two br. d, *J* = 13.5, NH)]*[2]
3h	1728-1710, 1686, 1638	3080	1.32 (3H, t, *J* = 7, CH_3); 1.36 (3H, t, *J* = 7, CH_3); 4.28 (2H, q, *J* = 7, CH_2); 4.51 (2H, q, *J* = 7, CH-2); 7.27-8.11 (4H, m, Ar); 8.63 (1H, d, *J* = 14, =CH–); 14.58 (1H, br. d, *J* = 14, NH)
5a	1694	3220	6.69 (1H, d, *J* = 8, CH); 6.96 (1H, d. t, *J* = 7, *J* = 2, Ar); 7.12 (1H, d, *J* = 8, OH); 7.14-7.85 (5H, m, Ar); 8.24 (1H, dd, *J* = 7, *J* = 2, Ar); 8.35 (1H, dd, *J* = 8, *J* = 2, Ar)
5b	1692		0.97 (3H, t, *J* = 7, CH_3); 3.42 (2H, q, *J* = 7, CH_2); 6.71 (1H, s, CH); 7.29-7.67 (4H, m, Ar); 7.81 (1H, dd, *J* = 9, *J* = 2.5, Ar); 8.18 (1H, dd, *J* = 8, *J* = 2,5, Ar); 8.51 (1H, d, *J* = 2.5, Ar)

* The spectra were recorded in deuterochloroform (compounds **2a**,**b**,**h**,**k-m**, **3c**,**h**, **5b**) and DMSO-d_6 (compounds **2c-g**,**i**,**j**, **3a**,**b**,**d-g**, **5a**).
*[2] The spectrum was recorded in deuterochloroform.

TABLE 3. Bond Lengths (*l*) in the Structures of Compounds **2h**, **5a**, and **5b**

2h		**5a**		**5b**	
Bond	*l*, Å	Bond	*l*, Å	Bond	*l*, Å
1	2	3	4	5	6
O(1)–C(2)	1.383(3)	O(1)–C(2)	1.380(6)	O(1)–C(2)	1.393(10)
O(1)–C(9)	1.384(3)	O(1)–C(9)	1.373(6)	O(1)–C(9)	1.386(9)
C(2)–C(3)	1.414(4)	C(2)–C(3)	1.419(7)	C(2)–C(3)	1.433(9)
O(2)–C(11)	1.220(3)	C(2)–O(11)	1.237(6)	C(2)–O(11)	1.210(9)
C(3)–C(4)	1.410(3)	C(3)–C(4)	1.367(7)	C(3)–C(4)	1.366(10)
C(3)–C(12)	1.445(3)	C(3)–C(12)	1.482(7)	C(3)–C(12)	1.489(11)
C(4)–C(10)	1.463(3)	C(4)–C(10)	1.473(7)	C(4)–C(10)	1.460(10)
C(4)–N(14)	1.337(3)	C(4)–N(19)	1.364(6)	C(4)–N(19)	1.358(8)

TABLE 3 (continued)

1	2	3	4	5	6
C(5)–C(6)	1.370(3)	C(5)–C(6)	1.372(8)	C(5)–C(6)	1.389(12)
C(5)–N(10)	1.404(4)	C(5)–C(10)	1.394(7)	C(5)–C(10)	1.403(10)
C(6)–C(7)	1.388(4)	C(6)–C(7)	1.382(8)	C(6)–C(7)	1.388(13)
C(7)–C(8)	1.376(5)	C(7)–C(8)	1.386(8)	C(7)–C(8)	1.383(13)
C(8)–C(9)	1.389(4)	C(8)–C(9)	1.378(7)	C(8)–C(9)	1.376(12)
C(9)–C(10)	1.389(4)	C(9)–C(10)	1.392(7)	C(9)–C(10)	1.384(9)
C(12)–O(13)	1.220(3)	C(12)–N(13)	1.480(7)	C(12)–N(13)	1.491(7)
N(14)–C(15)	1.431(3)	C(12)–O(20)	1.403(6)	C(12)–O(20)	1.423(9)
C(15)–C(16)	1.360(4)	N(13)–C(14)	1.377(7)	N(13)–C(14)	1.376(9)
C(15)–C(24)	1.401(4)	N(13)–C(18)	1.371(6)	N(13)–C(18)	1.382(8)
C(16)–C(17)	1.425(4)	C(14)–C(15)	1.340(8)	C(14)–C(15)	1.339(11)
C(17)–C(18)	1.408(4)	C(15)–C(16)	1.395(8)	C(15)–C(16)	1.407(10)
C(17)–C(22)	1.421(4)	C(16)–C(17)	1.345(8)	C(15)–Cl(23)	1.721(8)
C(18)–C(19)	1.404(6)	C(17)–C(18)	1.431(7)	C(16)–C(17)	1.348(11)
C(19)–C(20)	1.375(6)	C(18)–N(19)	1.347(6)	C(17)–C(18)	1.417(9)
C(20)–C(21)	1.333(6)			C(18)–N(19)	1.322(9)
C(21)–C(22)	1.419(4)			O(20)–C(21)	1.444(10)
C(22)–C(23)	1.407(4)			C(21)–C(22)	1.48 (2)
C(24)–C(23)	1.366(4)				

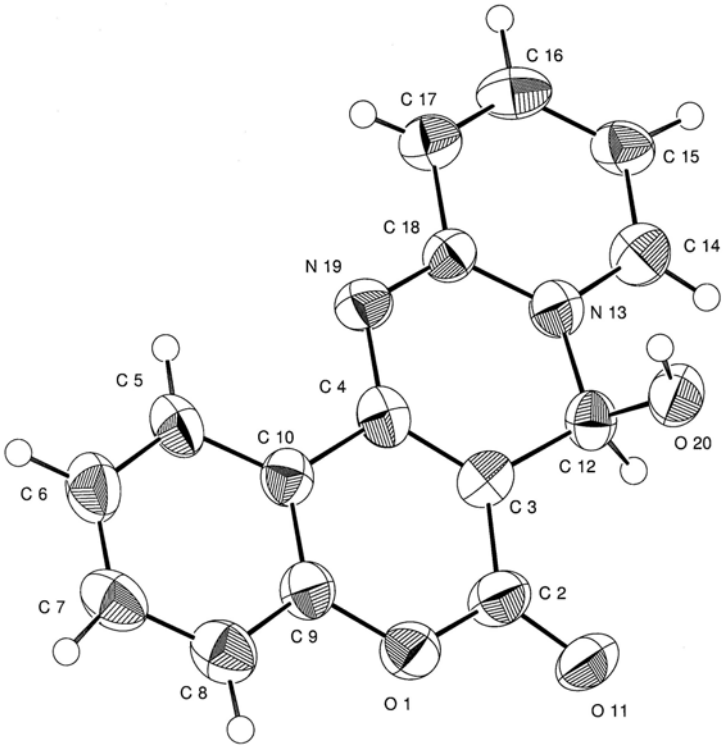


Fig. 2. Three-dimensional model of the **5a** molecule.

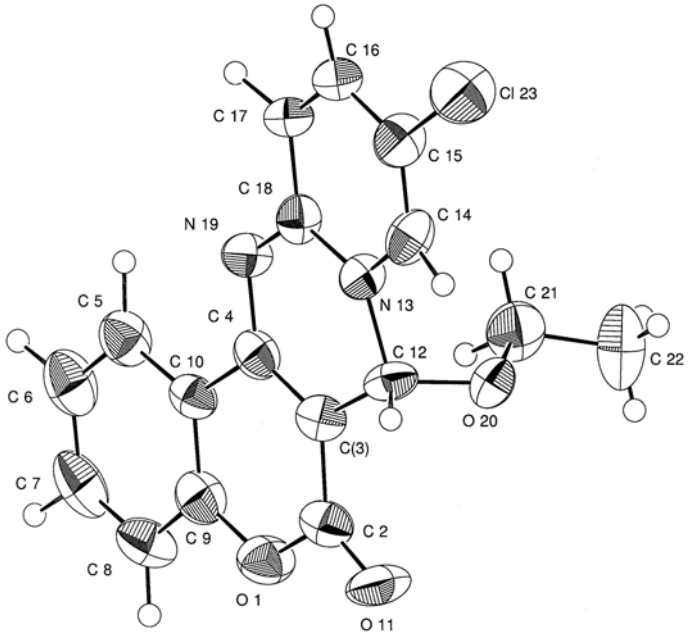


Fig. 3. Three-dimensional model of the **5b** molecule.

TABLE 4. The Crystallographic Data for Compounds **2h**, **5a**, and **5b**

Characteristic	**2h**	**5a**	**5b**
Empirical formula	$C_{20}H_{13}NO_3$	$C_{15}H_{10}N_2O_3$	$C_{17}H_{13}ClN_2O_3$
Molecular mass	315.33	266.26	328.74
Color of crystals	Colorless	Yellow	Colorless
Size, mm	0.02×0.11×0.26	0.04×0.06×0.52	0.01×0.24×0.30
Crystal system	Monoclinic	Monoclinic	Monoclinic
Crystal lattice parameters:			
a, Å	12.7109(6)	7.3933(8)	10.849(1)
b, Å	7.1408(4)	18.391(2)	18.837(2)
c, Å	18.153(1)	9.946(1)	7.6779(5)
β, deg	111.869(3)	120.577(5)	108.118(3)
Volume of unit cell, *V*, Å^3	1529.1(2)	1164.3(3)	1491.2(2)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Number of molecules in unit cell, *Z*	4	4	4
Density, *d*, g/cm^3	1.370	1.519	1.464
Absorption coefficient, μ, mm^{-1}	0.09	0.11	0.27
Number of unique reflections	4201	3167	2184
Number of reflections with $I > 3\sigma(I)$	1230	798	1003
Number of refined parameters	269	190	260
Final divergence factor, *R*	0.053	0.067	0.051

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Bruker WH 90/DS (90 MHz) and Varian Mercury BB (200 MHz) spectrometers with TMS as internal standard. The IR spectra were recorded on a Specord IR-75 instrument for suspensions of the substances in vaseline oil (1800-1500 cm^{-1}) and hexachlorobutadiene (3600-2000 cm^{-1}).

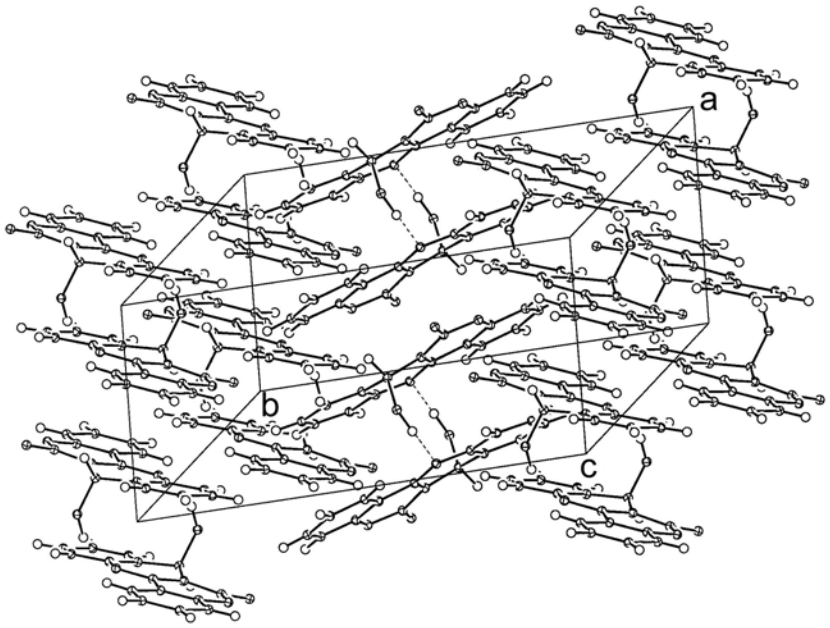


Fig. 4. The packing of the molecules in compound **5a**.

N-Monosubstituted 4-Amino-3-formylcoumarins 2a-l and 3-Aminomethylene-2,4-chromandiones 3a-e,g,h. To a boiling solution of the coumarin **1** (2 mmol) and triethylamine (4 mmol) in ethanol (10 ml) we added a boiling solution of the respective amine (or its hydrochloride) (2 mmol) in ethanol (10 ml). The mixture was boiled for 5 min and left at room temperature for 4-5 h. The precipitate was separated and recrystallized.

4-(2-Chloro-3-pyridyl)-3-formylcoumarin (2m) and 3-(2-Chloro-3-pyridyl)aminomethylene-2,4-chromandione (3f). A boiling solution of chlorocoumarin **1** (2 mmol) in ethanol (10 ml) was mixed with a solution of 3-amino-2-chloropyridine (2 mmol) in ethanol (10 ml). The mixture was boiled for 5 min and cooled. The precipitated 3-aminomethylene derivative **3f** was filtered off and recrystallized from a 3:2:1 mixture of DMF, ethanol, and water. The filtrate was diluted with water (50 ml), and the precipitated isomer **2m** was recrystallized from ethanol.

9-Chloro-7-ethoxy-6H,7H-[1]benzopyrano[4,3-*d*]pyrido[1,2-*a*]pyridin-6-one (5b). A boiling solution of coumarin **1** (2 mmol) in ethanol (10 ml) was mixed with a boiling solution of 2-amino-5-chloropyridine (2 mmol) and anhydrous sodium acetate (2 mmol) in ethanol (10 ml). The mixture was boiled for 5 min and cooled. The precipitated chromandione **3b** was filtered off and recrystallized from DMF–water. The yield was 22%. The filtrate was diluted with water (50 ml). The precipitated compound **5b** was filtered off and recrystallized from ethanol with the gradual addition of DMF. We obtained 0.33 g (50%) of compound **5b**.

7-Hydroxy-6H,7H-[1]benzopyrano[4,3-*d*]pyrido[1,2-*a*]pyridin-6-one (5a). The compound was obtained similarly from the coumarin **1** and 2-aminopyridine.

X-ray Crystallographic Analysis. Single crystals of compounds **2h**, **5a**, and **5b** were grown from DMF–ethanol. The diffraction patterns were recorded at 20°C on an automatic Nonius Kappa CCD diffractometer (MoKα radiation, for **2h** and **5a** $2\theta_{max} = 55°$, for **5b** $2\theta_{max} = 50°$). The structures were interpreted by the direct method and refined by full-matrix least-squares treatment in anisotropic approximation. The calculations were performed with the software in [9, 10].

The coordinates of the non-hydrogen atoms and their equivalent isotropic temperature parameters for compounds **2h**, **5a**, and **5b** can be obtained from the authors (e-mail: serg@osi.lv).

REFERENCES

1. A. Alberola, L. Calvo, A. Gonzalez-Ortega, A. P. Encabo, and S. Sanudo, *Synthesis*, 1941 (2001).
2. Ch. Bandyopadhyay, K. R. Sur, R. Patra, and A. Sen, *Tetrahedron*, **56**, 3583 (2000).
3. B. M. Bakulev, G. M. Gridunova, M. A. Kirpichenok, L. A. Karandashova, Yu. T. Struchkov, and I. I. Grandberg, *Khim. Geterotsikl. Soedin.*, 338 (1993).
4. D. Heber, *Arch. Pharm.*, **320**, 595 (1987).
5. S. R. Moorty, V. Sundaramurthy, and N. V. Subba Rao, *Indian J. Chem.*, **11**, 854 (1973).
6. I. Strakova, M. Petrova, S. Belyakov, and A. Strakovs, *Khim. Geterotsikl. Soedin.*, 1827 (2003) .
7. C. Giacovazzo (editor), *Fundamentals of Crystallography*, 2nd Ed., Oxford Sci. Publ., 590 (2002).
8. L. N. Kuleshova and P. M. Zorkii, *Acta Crystallogr.*, **B37**, 1363 (1981).
9. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, and R. Spagna, *J. Appl. Cryst.*, **32**, 115 (1999).
10. S. Mackay, C. J. Gilmore, C. Edwards, N. Stewart, and K. Shankland, *maXus, Computer Program for the Solution and Refinement of Crystal Structures*, Bruker Nonius, The Netherlands, MacScience, Japan, and The University of Glasgow (1999).