SYNTHESIS AND SPECTRAL AND LUMINESCENT PROPERTIES OF 3-FORMYL-7-DIALKYLAMINOCOUMARINS

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UDC 547.587.51

By means of the Vilsmeier reaction, starting with various 4-substituted 7-dialkylaminocoumarins having an open position 3, the corresponding 3-formyl derivatives have been obtained, and their spectral and luminescence characteristics have been studied. The ^{13}C NMR spectra and acid—base properties of a number of the synthesized compounds have been examined.

Certain representatives of 3-formyl-7-dialkylaminocoumarins are mentioned in the literature [1-3]. These compounds, which can be obtained by Vilsmeier formylation of 3-substituted coumarins, are valuable intermediates in the synthesis of luminophores fluorescing in the yellow—orange or orange—red regions of the visible spectrum [1, 2]. However, no detailed information has been reported on the properties of these aldehydes.

In order to define the specific features of the electronic influence of the 3-aldehyde group on the 7-aminocoumarin system, we synthesized a series of various 3-formyl-7-aminocoumarins and studied their spectral and luminescence characteristics as well as other physicochemical properties. As the starting materials we took a series of 7-dialkylaminocoumarins (I-X) in which the substituent in position 4 was varied, as well as the nature of the 7-amino group.

The formylation of compounds I-X was performed under standard conditions for the Vilsmeier reaction [4], by heating 1 g-eq of the 7-aminocoumarin with 1.5 to 2.5 g-eq of complexes of $POCl_3$ with DMFA. After heating for 2-6 h, the 3-formylcoumarins XI and XIII-XX were recovered from the reaction mixtures in good yields (Table 1) as the sole products.

An unexpected exception was the formylation reaction of the coumarin II. Under the usual conditions, the yield of the 3-formyl derivative was quite low; and even at low conversions (<50%), the yield was no higher than 30%. In this case, when the reaction mixture was treated with ammonia, we also recovered the coumarin XXI, the

TABLE 1. Physicochemical Characteristics of Coumarins XI-XXI

Compound	Empirical formula	mp, °C	R_f*	IR spectrum, $\nu_{C=O}$, cm^{-1}	Yield, %
XI	$C_{14}H_{15}NO_3$	163**	0,28	1725, 1685	87
XII	$C_{15}H_{17}NO_3$	159	0,23	1710, 1675	74
XIII	$C_{14}H_{14}ClNO_3$	139	0,44	1725, 1690	92
XIV	$C_{18}H_{22}N_2O_4$	182	0,13	1690	89
XV	$C_{21}H_{22}N_2O_3$	171	0,42	1705	85
XVI	$C_{14}H_{12}ClNO_4$	185	0,16	1750, 1660	78
XVII	$C_{18}H_{20}N_2O_5$	222	0,04	1690, 1665	82
XVIII	$C_{16}H_{15}NO_5$	203	0,15	1700, 1670	91
XIX	$C_{17}H_{17}NO_3$	233	0,20	1695, 1665	86
XX	$C_{16}H_{14}ClNO_3$	214	0,33	1740, 1710	90
XXI	$C_{17}H_{16}N_2O_3$	229	0,32	1735, 1690	70

*Values of R_f were obtained on Silufol UV-254 plates in a hexane—acetone system, 3:1.

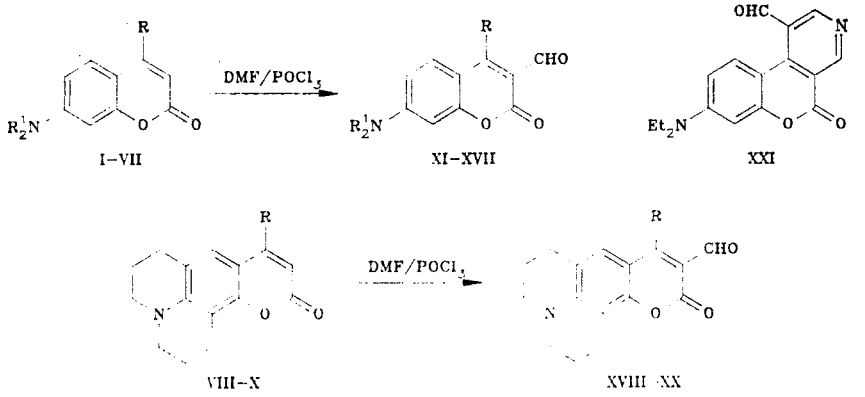
**According to [3], mp 160-162°C.

K. A. Timiryazev Moscow Agricultural Academy, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1480-1487, November, 1991. Original article submitted October 17, 1990.

0009-3122/91/2711-1193$12.50

yield of which could be increased to 70% by prolonged heating in an excess of the formylating agent. The formation of compound XXI indicates formylation of the 4-CH_3 group, and it has precedents in a number of acyclic compounds [5, 6]. In the PMR spectrum of the coumarin XXI, in addition to the usual signals of the coumarin protons in the weak fields, three singlet signals of the formylpyridine fragment are observed. In the mass spectrum of the aldehyde XXI there is an intense peak of the molecular ion (m/z 296). Fragmentation of compound XXI under electron impact confirms the presence of the coumarin structure, as indicated by the characteristic fragment ions related to dehydration of the 7-diethylamino group: $[M - CH_3]^+$ (m/z 291) and $[M - CH_3 - CO - CHO - HCN - C_2H_5]^+$ (m/z 168) [7]. Along with this, the elimination (nontypical for 7-aminocoumarins) of CO and HCN particles in the early stages of fragmentation — $[M - CH_3 - CO]^+$ (m/z 253), $[M - CH_3 - CO - CHO]^+$ (m/z 224), $[M - CH_3 - CO - CHO - HCN]^+$ (m/z 197) — is consistent with the presence of an additional carbonyl group and a nitrogen-containing hetero ring.

For the directed synthesis of the coumarin XII, we used the reaction of oxidation of the known [8] 3-hydroxymethyl-4-methyl-7-diethylaminocoumarin by manganese dioxide in benzene. The preparative yield of the aldehyde XII under these conditions was 74%.



I, VIII, XI, XVIII R=H, II, IX, XII, XIX R=CH_3; III, VI, X, XIII, XVI, XX R=Cl; IV, VII, XIV, XVII R=$N(CH_2CH_2)_2O$; V, XV R=$NHCH_2C_6H_5$; I–V, XI–XV R^1=C_2H_5; VI, VII, XVI, XVII NR_2^1=$N(CH_2CH_2)_2O$

Compounds XI-XX are bright yellow or red crystalline products with IR spectra exhibiting one or two bands of carbonyl absorption by aldehyde and lactone groups at 1660-1750 cm^{-1} (see Table 1). In the PMR spectra of compounds XI-XX (Tables 2 and 3), in addition to the signals of the coumarin protons [9], signals of aldehyde group protons are registered in the 10 ppm region.

TABLE 2. PMR Spectra of Coumarins XI-XVII

Compound	Chemical shifts, δ, ppm (SSCC, J, Hz)						
	5-H (d, J=9,0)	6-H (d.d, J=9,0, J=2,7)	8-H (d, J=2,7)	CHO, s	7-NCH_2 (q, J=7,0)	7-NCH_2CH_2R (t, J=7,0)	Other protons
XI	7,42	6,68	6,50	10,12	3,45	1,23	8,25 (1H, s, 4-H)
XII	7,65	6,67	6,43	10,37	3,44	1,22	2,80 (3H, s, CH_3)
XIII	7,80	6,69	6,40	10,25	3,47	1,25	—
XIV	7,60	6,55	6,41	10,00	3,41	1,20	3,60 (4H, t, J=5,1, *cyclo*-$N(CH_2)_2$); 3,95 (4H, t, J=5,1, *cyclo*-$O(CH_2)_2$)
XV	7,70	6,45	6,40	10,02	3,38	1,18	4,95 (2H, d., J=5,1, $CH_2C_6H_5$), 7,37 (5H, m, C_6H_5); 12,01 (1H, bt. t, J=5,1, NH)
XVI	7,88	6,76	6,60	10,28	3,55*	3,87*	—
XVII	7,68	6,75	6,60	10,03	3,60*	3,95*	3,31 (4H, t, J=5,0, $N(CH_2)_2$); 3,82 (4H, t, J=5,0, $O(CH_2)_2$)

*Triplet (J = 5.1 Hz).

TABLE 3. PMR Spectra of Coumarins XVIII-XX

Compound	Chemical shifts, δ, ppm (SSCC, J, Hz)					
	1-CH_2, 7-CH_2 (t, J=6,5)	2-CH_2, 6-CH_2, m	3-CH_2, 5-CH_2, m	8-H, s	9-R, s	10-CHO, s
XVIII	2,88; 2,76	1,96	3,37	6,95	8,10	10,09
XIX	2,90; 2,77	2,00	3,35	7,22	2,75	10,39
XX	2,86; 2,75	1,95	3,37	7,40	—	10,24

TABLE 4. Spectral and Luminescent Properties of 3-Formyl-7-aminocoumarins XI-XXI

Compound	Solvent	UV spectrum, λ_{max}, nm (log ε)	Fluorescence	
			λ_{max}	φ_f*
XI	C_2H_5OH	246 (3,86), 267 (3,93), 294 (3,70), 315 (3,26), 446 (4,72)	494	<0,10
	CH_3CN	241 (3,77), 266 (3,92), 294 (3,56), 315 (3,14), 443 (4,67)	489	<0,10
XII	C_2H_5OH	245 (3,93), 268 (3,94), 291 (3,63), 309 (3,29), 436 (4,74)	490	<0,10
	CH_3CN	246 (3,96), 263 (3,99), 291 (3,39), 312 (3,27), 432 (4,74)	486	<0,10
XIII	C_2H_5OH	249 (4,02), 265 (3,78), 300 (3,66), 449 (4,65)	502	<0,10
	CH_3CN	249 (3,84), 270 (3,89), 300 (3,51), 446 (4,57)	500	<0,10
XIV	C_2H_5OH	240 (4,14), 284 (3,87), 318 (3,78), 409 (4,57)	475	<0,10
	CH_3CN	240 (4,01), 284 (3,70), 320 (3,68), 405 (4,51)	475	<0,10
XV	C_2H_5OH	243 (4,40), 260 (4,04), 274 (3,94), 305 (3,96), 320 (3,91), 379 (4,74)	460	<0,10
	CH_3CN	240 (4,30), 260 (4,02), 274 (3,91), 307 (3,93), 320 (3,89), 378 (4,71)	460	<0,10
XVI	C_2H_5OH	249 (4,11), 290 (3,68), 393 (4,25), 435 (4,49)	500	<0,10
	CH_3CN	253 (4,00), 264 (4,00), 290 (3,65), 430 (4,60)	504	<0,10
XVII	C_2H_5OH	250 (4,19), 345 (4,78), 392 (4,54)	480	<0,10
	CH_3CN	244 (4,25), 276 (3,80), 309 (3,80), 388 (4,16)	470	<0,10
XVIII	C_2H_5OH	282 (3,84), 301 (3,85), 469 (4,43)	510	0,48
	CH_3CN	277 (3,88), 299 (3,83), 461 (4,47)	504	0,47
XIX	C_2H_5OH	276 (3,75), 287 (3,72), 299 (3,68), 454 (4,57)	508	0,81
	CH_3CN	275 (4,05), 287 (3,96), 298 (3,91), 450 (4,81)	504	0,77
XX	C_2H_5OH	255 (3,80), 283 (3,93), 300 (3,88), 468 (4,64)	520	<0,10
	CH_3CN	282 (3,97), 300 (3,90), 465 (4,71)	515	<0,10
XXI	C_2H_5OH	259 (3,99), 305 (3,54), 312 (3,64), 380 (4,32)	525	<0,10
	CH_3CN	258 (4,18), 306 (3,45), 317 (3,45), 394 (4,52)	560	<0,10

*φ_f is the quantum yield.

In the electronic spectra of the aldehydes XI-XX in ethanol or acetonitrile (Table 4), the long-wave absorption maximum is shifted bathochromically in comparison with the original coumarins I-X by 30-70 nm [10-12]. A similar trend is observed when electron-acceptor groups are introduced into the pyrone ring of 7-aminocoumarins [13], and it is related to an increase in charge transfer in such systems. Analysis of the relative changes in the absorption spectra of the coumarins XI-XV in comparison with the coumarins I-V shows that the shift of the long-wave maximum increases in the following order in the series of structurally related pairs of compounds: V, XV ($\Delta\lambda \sim 30$ nm) < IV, XIV ($\Delta\lambda \sim 45$ nm) < II, XII ($\Delta\lambda \sim 60$ nm) ≈ III, XIII ($\Delta\lambda \sim 60$ nm) < I, XI ($\Delta\lambda \sim 70$ nm). On the other hand, in this same series, for the aldehydes XI-XV, we observe a bathochromic shift of the absorption maximum. Both trends are evidently due to a decrease in charge transfer in state S_0 from the 7-diethylamino group to the pyrone ring as the electron-donor strength of the substituent in position 4 is increased (see also [10]), which is the greatest in the coumarin XV. Similar relationships can be followed for the other formyl derivatives that have been studied.

The coumarins XI-XVII and XX exhibit weak fluorescence, and the coumarins XVIII and XIX intense fluorescence, in the 460-520 nm interval (see Table 4). The quenching of fluorescence for aldehydes with an unanchored 7-dialkylamino group may be related to transformation of a ST state into a nonfluorescing TIST state [4]. The low fluorescence of the chloro derivative XX is also characteristic for other 4-chloro-7-aminocoumarins [11]. The electronic influence of substituents on the position of the emission maximum for compounds XI-XX is not

TABLE 5. ^{13}C NMR Spectra of Coumarins I-IV and XI-XIV

Compound	Empirical formula, δ, ppm (SSCC, J ^{13}C, ^{1}H, Hz)												
	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(4a)}$, m	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(8a)}$	7-NCH_2	7-NCH_2CCH_3	Other carbon atoms
I	162,0 (d.d., J=11,1; J=4,7)	108,8 (d J=171,9)	143,6 (d.d., J=160,9; J=4,8)	108,1	128,7 (d.d., J=159,8; J=4,9)	108,5 (d.d, J=159,7; J=5,7)	150,5 m	97,2 (d.d, J=159,9; J=5,4)	156,5 m	44,6 (t, J=135,6)	12,3 (q, J=126,6)	—
II*	161,4	108,2	152,1	109,2	125,4	109,0	150,4	97,8	156,1	44,7	12,6	18,4
III	160,2 (d, J=2,8)	107,5 (d, J=176,1)	149,7 m	106,5	126,1 (d, J=162,8)	108,8 (d.d, J=160,9; J=5,7)	151,4 m	96,7 (d.d, J=160,9; J=5,4)	155,3 (d.d, J=9,2; J=5,4)	44,6 (t, J=135,9)	12,2 (q, J=126,8)	—
IV**	163,2	92,3	161,7	104,0	125,5	107,8	150,0	97,7	156,5	44,4	12,3	51,3, 66,3
XI	160,5 (d, J=9,4)	113,0 (d, J=23,0)	144,9 (d, J=162,6)	107,2	131,8 (d.d. J=162,4; J=4,5)	109,5 (d.d, J=161,7; J=5,4)	152,7 m	96,0 d.d, (J=161,4; J=4,6)	157,9 m	44,3 (t, J=136,0)	11,5 (q, J=127,0)	186,4 (d.d, J=181,0; J=4,6)
XII	162,8 s	112,4 (dq J=22,0; J=3,6)	159,5 m	109,3	128,6 (d, J=160,3)	109,8 (d.d, J=161,1; J=5,5)	152,7	97,0 (d.d, J=161,1; J=5,3)	157,2 (d.d, J=9,3; J=5,7)	45,1 (tq J=136,7; J=3,9)	12,5 (q, J=127,0)	14,8 (q, J=129,6), 191,3 (q, J=182,4)
XIII	159,2 s	110,1 (d, J=24,1)	153,5 m	106,9	128,7 (d, J=164,5)	110,3 (d.d, J=162,4; J=6,0)	153,3 m	96,0 (d.d, J=162,1; J=5,1)	155,8 (d.d, J=8,7; J=5,5)	45,0 (tq J=136,9; J=4,3)	12,1 (q, J=127,5)	186,3 (d J=185,7)
XIV	160,2 s	101,8 (d, J=23,2)	164,9 m	104,6	128,6 (d, J=159,1)	108,8 (d.d, J=161,4; J=5,7)	151,6 m	97,6 (d.d, J=161,1; J=5,2)	157,2 (d.d, J=9,4; J=5,2)	44,7 (tq J=136,3; J=4,3)	12,3 (q, J=127,0)	54,0 (t, J=140,0), 66,9 (t, J=143,7), 186,9 (d, J=181,5)

*According to [9].
**According to [16].

TABLE 6. ^{13}C NMR Spectra of Coumarins X and XX

Compound	Chemical shifts, δ, ppm (SSCC, J ^{13}C, ^{1}H, Hz)															other carbon atoms
	$C_{(7a)}$, m	$C_{(8)}$, dt	$C_{(8a)}$	$C_{(9)}$, m	$C_{(10)}$, d	$C_{(11)}$ m	$C_{(12a)}$, m	$C_{(12b)}$, m	$C_{(12c)}$,	$C_{(1)}$,	$C_{(2)}$,	$C_{(3)}$,	$C_{(5)}$,	$C_{(6)}$,	$C_{(7)}$,	
X	118,8	122,5 (J=160,5; J=3,9)	106,7 (d, J=5,9)	150,2	107,1 (J=175,9)	161,0 (d, J=2,4)	150,6	106,3	146,9	20,5 (J=129,9)	20,5 (J=129,9)	49,6 (J=137,2)	50,0 (J=137,6)	21,3 (J=129,7)	27,7 (J=128,9)	—
XX	120,5	124,9 (J=162,2; J=3,8)	106,3 m	153,5	109,5 (J=24,2)	160,2 s	151,4	105,6	149,7	20,0 (J=130,8)	20,1 (J=130,0)	50,0 (J=138,8)	50,5 (J=139,7)	21,0 (J=130,0)	27,6 (J=129,7)	187,2 (, J=184,8)

as clear-cut as in the case of the absorption spectra, but the same trend remains toward a shift to shorter wavelengths with increasing electron-donor properties of the group in position 4. This leads in particular to an increase of the Stokes shifts in the series of 7-diethylamino derivatives XI < XIII ≈ XII < XIV < XV. No such effect is observed for the model coumarins I-V [10-12]. When the change is made from the coumarin V to the aldehyde XV, in contrast to the other related pairs of 7-aminocoumarins, the Stokes shift increases. This may be due to the presence of an intramolecular hydrogen bond in the molecule of XV, leading to additional stabilization of the CT state. In the present work, we have not brought in the possibility (in principle) of proton transfer and the existence of this compound in several tautomeric forms with an intramolecular hydrogen bond; this will be the subject of a separate publication.

In the example of the compounds we have studied, we can arrive at the conclusion that the electronic spectra of 3-formyl-7-aminocoumarins are rather sensitive to modification of the substituent in position 7. Thus, anchoring of a 7-diethylamino group in a morpholine ring when the change is made from the coumarins XIII and XIV to the coumarins XVI and XVII is accompanied by a significant shift of the absorption maximum toward shorter wavelengths ($\Delta\lambda_{max}^{ab}$ 14-17 nm); and a change, for example, from the 7-diethylamino derivatives XI-XIII to the julolidine analogs XVIII-XX has the opposite effect ($\Delta\lambda_{max}^{ab}$ 18-23 nm). These relationships are determined by the electron-donor strength of the dialkylaminobenzene fragment, which increases when the change is made from morpholino to diethylamino and then to the julolidino derivative.

Additional information on the electronic structure of the 3-formyl-7-aminocoumarins can be obtained from the ^{13}C NMR spectra of these compounds, since it is known [15] that the ^{13}C NMR chemical shifts for coumarins correlate well with the distribution of π-electron density. In Tables 5 and 6 we present ^{13}C NMR data for compounds XI-XIV and XX in comparison with the original 3-nonsubstituted coumarins. The assignment of signals was based on [9, 16]. The introduction of a strong acceptor — the formyl group — into position 3 of molecules I-III results in a significant downfield shift of the signals of the $C_{(3)}$—$C_{(5)}$ and $C_{(7)}$ atoms ($\Delta\delta$ 1.5-7.4 ppm) and very little change in the other chemical shifts, with the shielding of the $C_{(2)}$ atom increasing slightly ($\Delta\delta$ —1.0 to —1.5 ppm). Such an effect means that the entire 7-aminocoumarin π-system, including the most distant atom $C_{(7)}$ ($\Delta\delta$ ~2 ppm), is responding to the electron-acceptor action of the aldehyde group. An analogous effect is observed for the aldehyde XX in comparison with the coumarin IX. In the coumarin XIV, the influence of substituents on the chemical shifts of the $C_{(2)}$ and $C_{(3)}$ atoms is nonadditive. Thus, the signal of the $C_{(3)}$ atom in the aldehyde XIV, in comparison with the coumarin IV, undergoes a very marked downfield shift ($\Delta\delta$ 9.5 ppm); the signal of the $C_{(2)}$ atom is shifted upfield, and that of the $C_{(4)}$ atom downfield ($\Delta\delta$ —3.0 and 3.2 ppm, respectively). The indicated changes in the chemical shifts of the $C_{(2)}$ and $C_{(3)}$ atoms, by 2-7 ppm, are greater than the analogous changes in other related pairs; and they indicate steric interaction of the aldehyde and morpholino groups, leading to a decrease in their conjugation with the coumarin fragment.

We have made an independent evaluation of the electronic influence of the 3-formyl group on the 7-aminocoumarin fragment by studying the basicity of the coumarins XI-XIV and XVI in water—ethanol solutions

TABLE 7. Acid—Base Properties of Coumarins I-IV, XI-XIV, and XVI in Water—Ethanol Solutions

Compound	Absorption, λ_{max}, nm		pK_a	pK^*_a
	neutral molecule	monocation		
I*	390	311	1,79	—12,12
II*	385	310	1,97	—11,43
III	401	332	0,58	—10,55
IV**	373	309	1,86	—10,01
XI	450	333	—0,08	—16,77
XII	444	334	0,44	—15,40
XIII	456	333	—0,46	—17,79
XIV	415	320	0,46	—14,84
XVI	440	333	—1,67	—17,29

*According to [18].
**According to [10].

(Table 7). The primary protonation of these compounds takes place at the nitrogen atom in position 7, as indicated by the hypsochromic shift of the absorption maximum ($\Delta\lambda_{max} \sim 100$ nm) and the quenching of fluorescence upon acidification [10]. The values of pK_a of the conjugated acids of the coumarins XI, XII, and XIV show that their basicities are approximately 1.5 orders of magnitude lower than those of the original coumarins I, II, and IV (see Table 7). The difference of basicity is slightly smaller in the case of the 4-chloro derivatives III and XIII ($\Delta pk_a \sim 1$). In our opinion, this fact is explained by manifestation of mainly electron-acceptor properties by the Cl atom in the coumarin III (—I effect), whereas in the molecule of XIII, the analogous Cl atom is conjugated with the aldehyde group and can act to a greater degree as a donor of electron density (+M effect). As a result, the change from the coumarin III to the aldehyde XIII is not accompanied by as great an increase of charge transfer from the 7-diethylamino group as is the case in the pairs of molecules I and XI, II and XII, or IV and XIV. In any case, the aldehyde group in 3-formyl-7-aminocoumarin should be regarded as a strong electron acceptor. A calculation of values of pK_a* (see Table 7) by the method of Förster [17] indicates a sharp decrease in basicity of compounds XI-XIV and XVI upon excitation, which is characteristic for other 7-aminocoumarins as well [10, 12, 18].

EXPERIMENTAL

The IR spectra were obtained in a Perkin—Elmer 577 spectrophotometer in KBr tablets, the UV and fluorescence spectra in a Hitachi EPS-3T spectrophotometer with a G-3 luminescence attachment. The relative quantum yields of fluorescence were determined on the basis of Rhodamine 6G (φ_f 0.94) or 3-aminophthalimide (φ_f 0.60 [17]).

The PMR spectra ($CDCl_3$) and the ^{13}C NMR spectra were registered in a Bruker WM-250 instrument (internal standard HMDS). The mass spectra were obtained in a Varian MAT-311 mass spectrometer (ionizing voltage 70 eV).

The pK_a values were determined spectrophotometrically [19] in 50% ethanol. Sulfuric acid served as the donor of oxonium ions. The pH values were measured in an ÉV-74 universal ionometer with glass and calomel electrodes. The error in determining pK_a was ± 0.04.

The elemental analyses of compounds XI-XXI for C, H, and N were in agreement with the calculated values.

General Method for Obtaining Coumarins XI and XIII-XX. To a Vilsmeier complex obtained by stirring for 1 h at 20°C a 6-10 mmoles quantity of absolute DMFA and an equivalent quantity of freshly distilled $POCl_3$, a solution of 4 mmoles of the original 7-aminocoumarin (I, III-X) in 20-40 ml of absolute DMFA was added. The reaction mixture was stirred 2-6 h at 20-60° until the original coumarin disappeared (monitored by TLC). The solution was poured into 400 ml of ice water and left overnight at 5°C. The resulting precipitate was filtered off, thoroughly washed with water, and dried at a temperature no higher than 70°C. If necessary, the 3-formylcoumarin product was recrystallized from a hexane—acetone mixture.

3-Formyl-4-methyl-7-diethylamino-2-H-benzopyran-2-one (XII). To a solution of 4.7 mmoles of 3-hydroxymethyl-4-methyl-7-diethylaminocoumarin [8] in 50 ml of benzene, while stirring, 47.4 mmoles of freshly prepared manganese dioxide was added. The reaction mixture was stirred for 2 h and then filtered. The filtrate was vacuum-evaporated, and the residue was chromatographed on silica gel Silpearl UV-254, eluent benzene—ethyl acetate, 10:1. The chromatographically pure product was crystallized from a hexane—acetone mixture.

1-Formyl-8-diethylamino-5-H-[1]benzopyrano[3,4-c]pyridin-5-one (XXI). The coumarin XXI was synthesized by the same general method for obtaining 3-formyl-7-aminocoumarins, from 4.0 mmoles of coumarin II and 6.0 mmoles of $POCl_3$. The reaction mixture was poured into 400 ml of ice water and neutralized with ammonia to pH 7.0. The precipitate was filtered off and crystallized from ethyl acetate. Obtained 0.83 g (70%) of compound XXI. PMR spectrum ($CDCl_3$): 127 (6H, t, J = 7.0 Hz, 8-$N(CH_2CH_3)_2$); 3.48 (4H, q, J = 7.0 Hz, 8-$N(CH_2CH_3)_2$); 6.57 (1H, d, J = 2.7 Hz, 7-H); 6.67 (1H, dd, $J_{9,10}$ = 9.0 Hz, $J_{7,9}$ = 2.7 Hz, 9-H); 7.67 (1H, d, J = 9.0 Hz, 10-H); 9.07 (1H, s, 4-H); 9.51 (1H, s, 2H); 10.52 ppm (1H, s, CHO). Mass spectrum, m/z (I_{rel}, %, not less than 5%): M^+ 296 (43), 281 (100), 253 (20), 224 (5), 197 (5), 168 (5), 151 (21), 140 (10), 121 (13), 105 (11), 96 (13), 95 (12), 83 (15), 69 (24), 57 (52).

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