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SYNTHESIS AND LUMINESCENCE-SPECTRAL AND ACID—BASE CHARACTERISTICS OF 3-AMINOMETHYL-7-DIALKYLAMINOCOUMARINS

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A series of 3-aminomethyl-7-dialkylaminocoumarins were obtained as a result of the reactions of 7-diethylaminocoumarin, 4-methyl- and 4-chloro-7-diethylaminocoumarins, 4-methyl-7-pyrrolidinocoumarin, 4-methyl-7-piperidinocoumarin, 2,3,6,7-tetrahydro-1H,5H-quinolizino[9,9a,1-gh]coumarin, and 9-methyl-, 9-chloro-, and 9-morpholino-2,3,6,7-tetrahydro-1H,5H-quinolizino-[9,9a,1-gh]coumarins with formaldehyde and with a series of primary and secondary amines.

Known electrophilic substitution reactions in the 7-aminocoumarin series are mainly limited to examples of alkylation [1], halogenation [2], and formylation [3,4] and lead to the synthesis of 3-substituted derivatives. In the present work we examined the problem of introducing various aminomethyl groups at position 3 in order to obtain new luminophores, including water-soluble dyes, that could be found in the salts of such compounds. The particular interest in the luminescence-spectral characteristics of the 3-aminomethyl-7-aminocoumarins is due also to the fact that more rigid structures with an intramolecular hydrogen bond, can in principle be produced during the protonation of these substances, and this can in turn lead to an increase in the quantum yield of fluorescence [5].

As starting materials we used a series of 7-dialkylaminocoumarins (I-IX). Compounds (IV) and (V) were synthesized for the first time from 4-methyl-7-aminocoumarin by alkylation with 1,4-chlorobromobutane and 1,5-dibromopentane in DMFA solution in the presence of sodium bicarbonate (Tables 1-3). We used the Mannich reaction to introduce the aminomethyl group at position 3 [6]. tert-Butylamine, allylamine, benzylamine, piperidine, morpholine, N-methyloctadecylamine, and imidazole were brought into reaction with the coumarins (I-IX). The syntheses were conducted in acetic acid solution with the addition of 3 eq of formaldehyde in the form of formalin, and as a result the coumarins (X-XXVI) were obtained with yields of 60-95% (Table 1).

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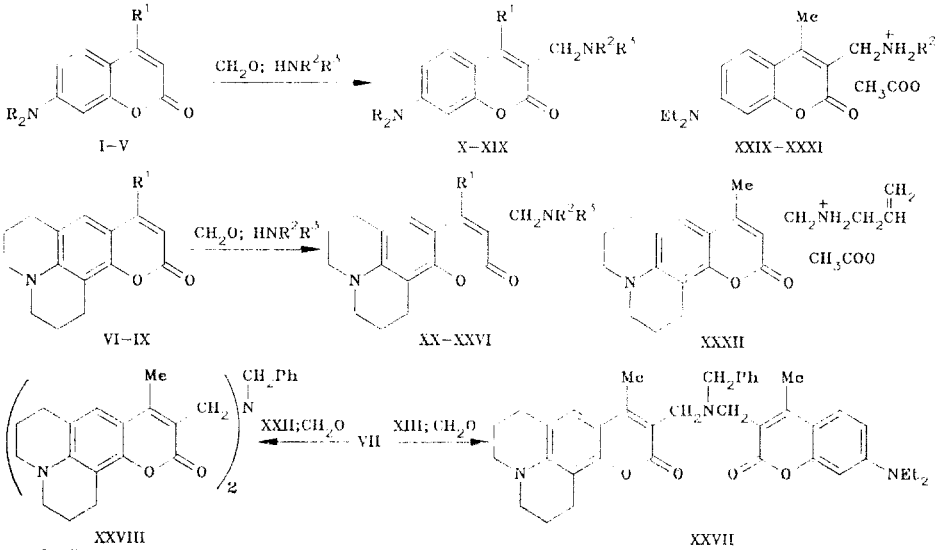
TABLE 1. Physicochemical Characteristics of the Coumarins (IV, V, X-XXXII)

Compound	Molecular formula	T_{mp} °C	R_f*	IR spectrum, $\nu_{C=O}$, cm^{-1}	Yield, %
IV	$C_{14}H_{15}NO_2$	185	0,42	1710	60
V	$C_{15}H_{17}NO_2$	123	0,48	1710	67
X	$C_{18}H_{24}N_2O_3$	113	0,16	1700	62
XI	$C_{19}H_{28}N_2O_2$	110	0,02	1695	70
XII	$C_{18}H_{24}N_2O_2$	58	0,08	1690	95
XIII	$C_{22}H_{26}N_2O_2$	70	0,08	1700	94
XIV	$C_{20}H_{28}N_2O_2$	105	0,10	1695	53
XV	$C_{19}H_{26}N_2O_3$	96	0,26	1700	70
XVI	$C_{18}H_{21}N_3O_2$	160	0,06	1690	57
XVII	$C_{18}H_{23}ClN_2O_3$	135	0,33	1715	73
XVIII	$C_{19}H_{24}N_2O_3$	136	0,26	1710	91
XIX	$C_{20}H_{26}N_2O_3$	141	0,27	1710	75
XX	$C_{20}H_{24}N_2O_3$	166	0,08	1700	81
XXI	$C_{20}H_{24}N_2O_2$	101	0,08	1700	68
XXII	$C_{24}H_{26}N_2O_2$	108	0,03	1695	66
XXIII	$C_{22}H_{26}N_2O_3$	154	0,06	1695	92
XXIV	$C_{36}H_{58}N_2O_2$	86	0,22	1700	72
XXV	$C_{20}H_{23}ClN_2O_3$	179	0,30	1705	69
XXVI	$C_{24}H_{31}N_3O_4$	193	0,18	1685	67
XXVII	$C_{39}H_{43}N_3O_4$	218	0,46	1695	36
XXVIII	$C_{41}H_{43}N_3O_4$	265 (decomp.)	0,14	1695	16
XXIX	$C_{21}H_{32}N_2O_4$	225 (decomp.)	0,05	1700	70
XXX	$C_{20}H_{28}N_2O_4$	102	0,05	1710	95
XXXI	$C_{24}H_{30}N_2O_4$	110	0,06	1710	94
XXXII	$C_{22}H_{28}N_2O_4$	141	0,04	1700	90

*The R_f values were measured on Silufol UV plates in the 2:1 hexane—acetone system.



I—III, X—XVII R=C_2H_5; IV, XVIII NR_2=N$(CH_2)_4$; V, XIX NR_2=N$(CH_2)_5$; I, VI, X, XX R^1=H; II, IV, V, VII, XI—XVI, XVIII, XIX, XIX—XXIV R^1=CH_3; III, VIII, XVII, XXV R^1=Cl; IX, XXVI R^1=N$(CH_2CH_2)_2$O; XI, XXIX R^2=*t*-C_4H_9; XII, XXI, XXX R^2=CH_2CH=CH_2; XIII, XXII, XXXI R^2=$CH_2C_6H_5$; XIV NR^2R^3=N$(CH_2)_5$; X, XV, XVII—XX, XXIII, XXV, XXVI NR^2R^3=N$(CH_2CH_2)_2$O; XVI NR^2R^3=N-imidazolyl: XXIV NR^2R^3=N$(CH_3)C_{18}H_{37}$; XI—XIII, XXI, XXII R^3=H

In the case of the primary amines traces of the bisadducts involving two molecules of coumarin were detected in the reaction mixtures according to the PMR data. In order to confirm this more rigorously compounds (XXVII) and (XXVIII) were synthesized from the coumarins (XIII) and (XXI) and identified. In order to investigate the possibility of obtaining water-soluble luminophores from the coumarins (XI-XIII, XXI) the acetates (XXIX-XXXII) were also isolated. We note that the coumarins (XII, XXI, XXX, XXXII) are prospective intermediates for the

TABLE 2. Luminescence-Spectral Characteristics of the Coumarins (IV, V, X-XXXII)

Compound	Solvent	Absorption, λ_{max}^{ab}, nm (log ε)	Fluorescence	
			λ_{max}^{em}, nm	φ_f*
IV	C_2H_5OH	278 (3,51), 303 (3,71), 314 (3,81), 374 (4,55)	460	0,73
	CH_3CN	278 (3,32), 303 (3,70), 314 (3,85), 369 (4,58)	448	0,80
V	C_2H_5OH	303 (4,27), 365 (4,27)	460	0,66
	CH_3CN	303 (3,60), 360 (4,32)	448	0,77
X	C_2H_5OH	255 (4,12), 281 (3,28), 308 (3,45), 322 (3,58), 385 (4,44)	470	0,33
	CH_3CN	255 (4,06), 309 (3,50), 3,22 (3,09), 374 (4,45)	456	0,32
XI	C_2H_5OH	250 (4,23), 281 (3,42), 307 (3,53), 317 (3,66), 382 (4,46)	462	0,44
	CH_3CN	254 (4,19), 281 (3,42), 307 (3,66), 318 (3,62), 377 (4,46)	462	0,35
XII	C_2H_5OH	250 (4,22), 279 (3,48), 303 (3,56), 315 (3,62), 380 (4,44)	462	0,42
	CH_3CN	251 (4,11), 279 (3,32), 305 (3,56), 316 (3,68), 370 (4,39)	454	0,43
XIII	C_2H_5OH	250 (4,20), 279 (3,47), 305 (3,56), 315 (3,59), 380 (4,42)	460	0,63
	CH_3CN	256 (4,14), 281 (3,37), 303 (3,57), 316 (3,68), 373 (4,40)	460	0,51
XIV	C_2H_5OH	253 (4,19), 281 (3,44), 305 (3,49), 316 (3,58), 380 (4,43)	460	0,16
	CH_3CN	251 (4,13), 281 (3,36), 303 (3,66), 316 (3,67), 374 (4,41)	460	0,09
XV	C_2H_5OH	254 (4,22), 281 (3,44), 307 (3,57), 317 (3,62), 382 (4,48)	460	0,41
	CH_3CN	251 (4,15), 280 (3,35), 308 (3,59), 317 (3,69), 374 (4,45)	454	0,55
XVI	C_2H_5OH	252 (4,22), 281 (3,44), 305 (3,49), 317 (3,52), 388 (4,48)	466	0,47
	CH_3CN	253 (4,14), 281 (3,36), 306 (3,52), 317 (3,58), 379 (4,46)	458	0,56
XVII	C_2H_5OH	251 (4,23), 256 (4,20), 281 (3,47), 306 (3,41), 317 (3,44), 392 (4,47)	475	—
	CH_3CN	253 (4,24), 283 (3,49), 306 (3,53), 317 (3,61), 386 (4,53)	474	—
XVIII	C_2H_5OH	251 (4,12), 279 (3,37), 290 (3,30), 312 (3,17), 325 (3,24), 379 (4,31)	462	0,56
	CH_3CN	250 (4,09), 279 (3,23), 296 (3,36), 305 (3,50), 316 (3,60)	450	0,38
XIX	C_2H_5OH	305 (3,62), 369 (4,38)	464	0,51
	CH_3CN	289 (3,62), 361 (4,39)	455	0,39
XX	C_2H_5OH	252 (3,91), 266 (3,86), 303 (3,61), 315 (3,64), 398 (4,35)	484	0,74
	CH_3CN	250 (3,89), 263 (3,82), 286 (3,43), 316 (3,43), 331 (3,57), 380 (4,31)	470	0,63
XXI	C_2H_5OH	253 (3,97), 270 (3,82), 286 (3,51), 312 (3,32), 397 (4,33)	480	0,82
	CH_3CN	249 (3,91), 267 (3,73), 282 (3,45), 312 (3,39), 386 (4,23)	478	0,74
XXII	C_2H_5OH	252 (4,06), 286 (3,66), 312 (3,48), 322 (3,48), 395 (4,36)	494	0,80
	CH_3CN	250 (4,06), 286 (3,60), 312 (3,49), 322 (3,56), 389 (4,37)	490	0,71
XXIII	C_2H_5OH	252 (4,09), 286 (3,72), 312 (3,47), 395 (4,39)	486	0,84
	CH_3CN	249 (4,07), 286 (3,63), 312 (3,53), 322 (3,57), 389 (4,37)	478	0,63
XXIV	C_2H_5OH	252 (4,14), 287 (3,73), 319 (3,60), 397 (4,44)	482	0,45
	CH_3CN	252 (4,06), 287 (3,76), 314 (3,54), 405 (4,35)	482	0,72
XXV	C_2H_5OH	261 (4,27), 292 (3,90), 318 (3,36), 410 (4,52)	486	<0,10
	CH_3CN	254 (4,08), 263 (4,00), 291 (3,53), 318 (3,29), 405 (4,47)	484	<0,10
XXVI	C_2H_5OH	252 (3,96), 265 (3,98), 282 (3,86), 316 (3,91), 392 (4,36)	484	0,44
	CH_3CN	251 (4,02), 278 (3,89), 317 (3,94), 386 (4,36)	484	0,38
XXVII	C_2H_5OH	251 (4,56), 286 (3,99), 304 (3,93), 310 (3,98), 391 (4,80)	478	0,22
	CH_3CN	247 (4,63), 285 (3,99), 317 (4,08), 382 (4,85)	470	0,08
XXVIII	C_2H_5OH	250 (4,27), 287 (3,92), 309 (3,80), 392 (4,51)	480	0,13
	CH_3CN	287 (3,89), 308 (3,81), 388 (4,41)	470	0,11
XXIX	C_2H_5OH	258 (4,17), 282 (3,34), 306 (3,41), 389 (4,44)	462	0,46
	CH_3CN	250 (4,22), 281 (3,48), 306 (3,53), 317 (3,55), 391 (4,52)	462	0,31
XXX	C_2H_5OH	250 (4,20), 281 (3,28)), 306 (3,41), 315 (3,48), 383 (4,44)	464	0,72
	CH_3CN	259 (4,21), 281 (3,31), 304 (3,56), 317 (3,68), 370 (4,51)	464	0,33
XXXI	C_2H_5OH	251 (4,13), 281 (3,31), 305 (3,43), 316 (3,48), 382 (4,36)	460	0,46
	CH_3CN	250 (4,10), 278 (3,29), 305 (3,52), 317 (3,63), 372 (4,38)	450	0,49
XXXII	C_2H_5OH	251 (4,07), 267 (3,99), 286 (3,72), 312 (3,56), 398 (4,38)	480	0,91
	CH_3CN	249 (4,12), 273 (3,82), 286 (3,67), 311 (3,59), 385 (4,32)	474	0,77

*φ_f is the relative quantum yield of fluorescence.

TABLE 3. PMR Spectra of the Coumarins (IV, V, X-XIX, XXIX-XXXI) in Deuterochloroform

Compound	Chemical shifts, δ, ppm (SSCC, Hz)							
	5-H (d, J=9,0)	6-H (d.d, J=9,0; J=2,6)	8-H (d, 2,6)	3-CH_2 (c)	4-R' (c)	7-NCH_2 (J=7,0)	7-NCH_2CH_2R (J=7,0)	other protons
IV	7,38	6,48	6,32	5,92*	2,32	3,33 m	2,04 m	—
V	7,37	6,61	6,50	5,92*	2,33	3,50 t**	1,78 m	1,55 (2H, m $N(CH_2CH_2)_2\mathbf{CH_2}$)
X	7,25	6,58	6,51	3,44	7,60	3,42 q	1,22 t	2,55 (4H, m $N(CH_2)_2$); 3,74 (4H, m $O(CH_2)_2$)
XI	7,39	6,57	6,47	3,69	2,41	3.39 q	1,20 t	1,23 (9H, s $C(CH_3)_3$); 2,95 (1H, m NH)
XII	7,42	6,60	6,49	3,79	2,42	3,41 q	1,20 t	2,55 (1H, m NH); 3,33 (2H, m CH_2C=); 5,19 (2H, m CH=$\mathbf{CH_2}$); 5,95 (1H, m, $C\mathbf{H}$=CH_2)
XIII	7,41	6,59	6,49	3,83	2,31	3,41q	1,21t	2,10 (1H, s NH); 3,76 (2H, s CH_2); 7,20...7,40 (5H, m C_6H_5)
XIV	7,42	6,58	6,46	3,49	2,43	3,40q	1,20t	1,20...1,50 (6H, m $(CH_2)_3$); 2,45 (4H, m $N(CH_2)_2$)
XV	7,43	6,59	6,45	3,57	2,46	3,40q	1,19t	2,57 (4H, m $N(CH_2)_2$); 3,70 (4H, m $O(CH_2)_2$)
XVI	7,42	6,60	6,47	5,11	2,43	3,41q	1,19t	7,00; 7,03 and 7,62 (1H each, bs, imidazolyl protons)
XVII	7,64	6,63	6,50	3,65	—	3,44q	1,20t	2,60 (4H, m $N(CH_2)_2$); 3,71 (4H, m $O(CH_2)_2$)
XVIII	7,47	6,49	6,34	3,50	2,42	3,33m	2,05m	2,50 (4H, m $N(CH_2)_2$); 3,69 (4H, m $O(CH_2)_2$)
XIX	7,46	6,62	6,50	3,52	2,43	3,32m	1,68m	1,68 (2H, m $N(CH_2CH_2)_2\mathbf{CH_2}$); 2,50 (4H, m $N(CH_2)_2$; 3,68 (4H, m $O(CH_2)_2$)
XXIX	7,44	6,60	6,50	4,07	2,67	3,42q	1,21t	1,60 (9H, s $C(CH_3)_3$); 1,98 (3H, s CH_3COO); 7,70 (2H, br.s, NH_2^+)
XXX	7,44	6,61	6,49	3,90	2,43	3,42q	1,22t	1,97 (3H, s CH_3COO); 3,45 (2H, m NCH_2C=); 5,20...5,35 (2H, bs C=CH_2); 5,95 (1H, m $C\mathbf{H}$=CH_2); 7,10 (2H, bs NH_2^+)
XXXI	7,44	6,61	6,49	3,98	2,36	3,42q	1,21t	1,99 (3H, s CH_3COO); 3,91 (2H, s CH_2); 7,11 (2H, bs NH_2^+); 7,26...7,40 (5H, m C_6H_5)

*Singlet of the 3-H proton.

TABLE 4. PMR Spectra of the Coumarins (XX-XXVIII, XXXII) in Deuterochloroform

Compound	Chemical shifts, δ, ppm (SSCC, Hz)							
	$C_{(1)}H_2$ (t J=6,5)	$C_{(2)}H_2$, $C_{(6)}H_2$ (m)	$C_{(3)}H_2$, $C_{(5)}H_2$ (m)	$C_{(7)}H_2$ (t J=6,5)	8-H, s	9-R	10-CH_2, s	other protons
XX	2,90	1,97	3,25	2,77	6,87	7,53 s	3,42	2,52 (4H, m, $N(CH_2)_2$); 3,73 (4H, m $O(CH_2)_2$)
XXI	2,89	1,96	3,24	2,77	7,02	2,35 s	3,74	3,20 (1H, s, NH); 3,25 (2H, m $\mathbf{CH_2}CH=CH_2$); 5,14 (2H, m, $C=\mathbf{CH_2}$); 5,91 (1H, m, $\mathbf{CH}=CH_2$)
XXII	2,91	1,98	3,26	2,79	7,03	2,30 s	3,82	2,05 (1H, s, NH); 3,78 (2H, s, $\mathbf{CH_2}C_6H_5$); 7,20...7,40 (5H, m C_6H_5)
XXIII	2,89	1,99	3,23	2,78	7,07	2,42 s	3,53	2,50 (4H, m, $N(CH_2)_2$); 3,65 (4H, m, $O(CH_2)_2$)
XXIV	2,89	1,97	3,22	2,79	7,04	2,42 s	3,47	1,22; 1,45 and 1,77 (36H, m, $C_{17}H_{36}$); 2,17 (3H, s NCH_3); 2,40 (2H, m, NCH_2)
XXV	2,87	1,98	3,27	2,80	7,25	—	3,66	2,60 (4H, m, $N(CH_2)_2$); 3,68 (4H, m, $O(CH_2)_2$)
XXVI	2,85	1,98	3,24	2,79	7,11	3,36 (t, J=4,6) 3,89 (t, J=4,6)	3,53	2,50 (4H, m, $N(CH_2)_2$); 3,67 (4H, m, $O(CH_2)_2$)
XXVII	2,87	1,97	3,22	2,78	6,99	2,22 s	3,62	1,19 (6H, t, J=7,0, $N(CH_2\mathbf{CH_3})_2$); 2,22 (3H, s $C_{(4)}-CH_3$); 3,40 (4H, q J=7,0, $N(\mathbf{CH_2}CH_3)_2$); 3,57 (2H, s, $\mathbf{CH_2}C_6H_5$); 3,62 (2H, $C'_{(3)}-CH_2$); 6,43 (1H, d 2,7,8′-H); 6,55 (1H, dd J=9,0, J=2,7, 6′-H); 7,10...7,30 (5H, m C_6H_5); 7,35 (1H, m J=9,0, 5′-H)
XXVIII	2,85	1,98	3,23	2,80	7,00	2,25 s	3,60	3,58 (2H, s $\mathbf{CH_2}C_6H_5$); 7,10...7,40 (5H, m C_6H_5)
XXXII	2,87	1,97	3,26	2,77	7,05	2,39 s	3,91	1,95 (3H, s CH_3COO^-); 3,42 (2H, m $\mathbf{CH_2}CH=CH_2$); 5,27 (2H, m, $C=CH_2$); 6,93 (2H, m NH_2^+)

TABLE 5. Acid—Base Characteristics of the Coumarins (X, XII, XIV-XVII, XX, XXII, XXIII) in 50% Ethanol

Compound	Absorption			Fluorescence		pK_a^I	pK_a^{II}	$(pK_a^I)^*$	$(pK_b^{II})^*$
	λ_{max}^{neut}	$\lambda_{max}^{K^+}$	$\lambda_{max}^{K^{2+}}$	λ_{max}^{neut}	$\lambda_{max}^{K^+}$				
X	395	408	315	477 (0,26)	482 (0,06)	5,92	1,04	7,63	−14,37
XII	385	397	313	471 (0,45)	475 (0,16)	8,30	1,24	10,01	−13,10
XIV	386	398	315	4,69 (0,21)	477 (0,11)	8,27	1,37	9,98	−12,75
XV	389	402	315	470 (0,41)	476 (0,10)	6,00	1,24	7,71	−13,31
XVI	394	398	313	474 (0,26)	478 (0,14)	6,11	1,30	6,75	−13,25
XVII	402	417	322	486 (0,10)	494 (0,10)	5,50	0,60	7,43	−14,38
XX	412	426	336	493 (0,94)	498 (0,94)	6,00	0,19	7,71	−13,67
XXII	402	416	328	490 (0,90)	495 (0,94)	7,72	0,02	9,65	−13,89
XXIII	405	420	328	489 (0,84)	494 (0,92)	6,21	0,16	8,14	−14,50

production of fluorescent films and glasses, while the coumarin (XXIV) containing a long aliphatic chain may be of interest for molecular electronics in the creation of Langmuir—Blodgett fluorescent films [7].

The structure of the synthesized compounds is confirmed by the data from the PMR spectra (Tables 3 and 4). Thus, the spectra of the coumarins (X-XIX, XXIX-XXXI) contain signals for the aromatic protons 5-H, 6-H, and 8-H in the region of 6.3-7.6 ppm, indicating the absence of any substituents at the ortho positions to the 7-dialkylamino group. The 8-H proton (δ 6.9-7.3 ppm) and the characteristic cycloalkyl protons of the julolidine fragment (δ 2.0-3.3 ppm) are easily identified in the spectra of the coumarins (XX-XXVIII, XXXII) [8]. The signals of the methylene protons attached to the $C_{(3)}$ atom $(C_{(10)})^*$ usually appear in the form of several broad singlets in the region of 3.4-3.9 ppm. In compound (XVI) the chemical shifts of the $CH_2—C_{(3)}$ protons are recorded in the downfield region as a result of the descreening effect of the imidazolyl group. In the case of the benzylamine derivatives (XIII, XXII, XXVII, XXVIII) it is possible to trace a small but steady effect from the screening of the 4(10)-methyl groups by the phenyl with their signals 0.1-0.2 ppm upfield from the other methyl derivatives. For the coumarins (XI-XIII, XXI, XXII) the chemical shifts of the NH protons lie in the region of 2.0-3.2 ppm, which indicates the absence of an intramolecular hydrogen bond in these compounds. The PMR data do not make it possible to reach a conclusion about an intramolecular hydrogen bond in the salts (XXIX-XXXII), since the signals for the protons of the NH_2^+ group are shifted downfield by not more than 5 ppm [9]. The presence of the positive charge in the acetates (XXIX-XXXII) also leads to a small downfield shift ($\Delta\delta \sim 0.1$ ppm) of the signals of the α-methylene protons.

Since the chemical shifts of the protons of the morpholine ring for the coumarins (X, XV, XVII-XX, XXIII, XXV) are found in two characteristic regions at 2.5 and 3.7 ppm, it is possible to assign the signals of each of the morpholino groups in the coumarin (XXVI). Analysis of the chemical shifts of the methylene protons attached to the nitrogen atom for the N-benzylamino derivatives (XIII, XXII, XXXI) and the protons of the coumarins (XXVI, XXVIII) also makes it possible to distinguish between the signals of the $CH_2—C_{(3)}$ groups and the signals of the benzylic methylene protons, which are found in a rather more upfield region (Tables 2 and 4).

In the electronic spectra of the investigated compounds (Table 3) there is a long-wave absorption maximum (λ_{max}^{ab}) in the region of 370-410 nm in ethanol and 360-405 nm in acetonitrile. It is known [10] that a general tendency that operates in the series of 7-aminocoumarins is a bathochromic shift of the absorption maximum with increase in the electron-withdrawing characteristics of the substituent in the pyrone ring and with increase in the electron-donating ability of the aminobenzene fragment. In fact, this relationship can be traced in the coumarins (X-XXXII) with variation of the substituent at position 4(10) — change of substituent in the series $N(CH_2CH_2)_2O \rightarrow CH_3 \rightarrow H \rightarrow Cl$ is accompanied by a general bathochromic shift of approximately 20 nm [e.g., cf. coumarins (XXVI, XXIII, XX, XXV)]. As expected [10,11], the transition from the 7-diethylamino derivatives to the julolidine analogs leads to a bathochromic shift of λ_{max}^{ab} by approximately 15 nm. It is interesting that substitution of the diethylamino group by a piperidine ring in the transition from the coumarin (XV) to the coumarin (XIX) is accompanied by an appreciable hypsochromic shift ($\delta\lambda_{max}^{ab} \sim 10$ nm) of the absorption maximum in contrast to the pyrrolidine derivative (XVIII). A similar effect is found in the initial coumarins (II, IV, V) (Table 3). Comparison of the absorption spectra of the coumarins (I-IX) [11,12] and the coumarins (X-XXVIII) makes it possible to reach the conclusion that the 3-aminomethyl group has a weak electron-withdrawing effect on the 7-aminocoumarin system — the bathochromic shift of λ_{max}^{ab} with the introduction of the given substituent amounts to ~3-11 nm. The electron-withdrawing effect of the substituent at position 3(11) increases somewhat in the transition from the coumarins (XI-XIII, XXI) to the corresponding salts (XXIX-XXXII) ($\Delta\lambda_{max}^{ab} \sim 3$ nm).

*Here and subsequently the numbers of the analogous C and H atoms in the julolidine derivatives are given in parentheses.

In ethanol and acetonitrile the coumarins (X-XXXII) fluoresce in the region of 450-486 nm (Table 2), and the tendencies observed in the changes of the emission maximum in these compounds are as a whole similar to the changes in the absorption spectra. The quantum yields of fluorescence (φ_f) of the julolidine derivatives with other conditions equal are higher than the φ_f values of other 7-dialkylaminocoumarins, e.g., cf. compounds (XX-XXIII) and (X, XII, XV, XVIII, XIX) (Table 2). The low quantum yields of fluorescence in the chlorocoumarins (XVII-XXV) agree with the analogous relationship for other 4-chloro-7-aminocoumarins [12]. The quenching of the fluorescence in the biscoumarins (XXVII, XXVIII), which can be regarded as bifluorophores [13], is fairly unusual. In contrast to the 4-aminomethyl derivatives of 7-aminocoumarins [14], monoprotonation of the investigated compounds is not accompanied by fluorescence quenching, as shown by the fairly high δ_f values for the salts (XXIX-XXXII). A possible reason for this is the formation of an intramolecular hydrogen bond between the NH^+ and C=O groups in the ST state, due to the more rigid structure of the dye. Thus, the coumarins (X-XXVIII) can probably be regarded as suitable intermediates for the production of water-soluble luminophores.

In view of the particular interest in water-soluble laser dyes it was desirable to evaluate the salt-forming capacity of the obtained aminomethyl derivatives. In this connection we studied the basicity of the coumarins (X, XII, XIV-XVII, XX, XXII, XXIII) in water—ethanol solutions (Table 5). As expected, initial protonation took place at the nitrogen atom of the substituent at position 3. This is confirmed by the appreciable long-wave shift of the absorption and emission maxima ($\Delta\lambda_{max}^{ab} \sim$ 4-15 nm, $\Delta\lambda_{max}^{em} \sim$ 4-8 nm) with retention of the fluorescence, which for the julolidine derivatives (XX, XXII, XXIII) becomes even stronger than in the neutral molecules. The pK_a^I values of the conjugate acids of the investigated 7-aminocoumarins lie in the region of 5.5-8.3 and, as shown by calculation of $(pK_a^*)^I$ according to Forster [15], increase for the majority of molecules in the excited state by 1.7-1.9 units. It is quite likely that the lactone carbonyl group, capable of forming an intramolecular hydrogen bond (see above), participates in the stabilization of the onium center in the ST state in the coumarins (X, XII, XIV, XV, XVII, XX-XXII, XXIII). The exception is the coumarin (XVI), where the shift of the absorption maximum ($\Delta\lambda_{max}^{ab} \sim$ 4 nm) and the increase of the basicity in the excited state ($\Delta pK_a \sim 0.7$) is substantially smaller. This anomaly is explained by the specific nature of the protonation of the coumarin (XVI), in which the most basic center is the $N_{(3)}$ atom of the imidazole ring [14].

Secondary protonation of the investigated coumarins affects the nitrogen atom at position 7 and leads to a marked hypsochromic shift of the absorption maximum and to fluorescence quenching ($\Delta\lambda_{max}^{ab} \sim$ 83-92 nm). The pK_a^{II} values are determined by the specific nature of the structure of the 7-dialkylamino group and, according to data in [11] for 7-diethylamino derivatives (X, XII, XIV-XVII), is 0.6-1.5 orders of magnitude higher than for the coumarins (XX, XXII, XXXIII) (Table 5). Determination of the $(pK_a^*)^{II}$ values indicates a marked decrease in the basicity during excitation, characteristic of other 7-N-protonated coumarins [11,14].

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer. The UV spectra and the fluorescence spectra were obtained on a Hitachi EPS-3T spectrophotometer fitted with a G-3 fluorescence attachment. The φ_f values were determined for 3-aminophthalimide by the method in [15]. The PMR spectra were recorded on a Bruker WM-250 instrument with HMDS as internal standard.

The pK_a values were determined by a spectrophotometric method [16] in 50% ethanol. The error in the determination of pK_a was ± 0.04. The proton donor was hydrochloric acid. The pH values were measured on a Universal ÉV-74 pH-meter with glass and calomel electrodes.

The elemental analyses (C, H, N) for compounds (IV, V, X-XXXII) agreed with the calculated data.

General Procedure for the Production of the Coumarins (IV, V). To a solution of 1.0 g (5.7 mmole) of 4-methyl-7-aminocoumarin in 15 ml of absolute DMFA we added 11.4 mmole of 1,4-chlorobromobutane or 1,5-dibromopentane respectively and 1.0 g (11.9 mmole) of finely dispersed sodium bicarbonate. The mixture was heated and stirred in a flask with a reflux condenser at 120-140°C for 15 h. The reaction mixture was evaporated under vacuum, the residue was dissolved in 15 ml of methylene chloride, and the solution was filtered. The filtrate was evaporated, the residue was separated by column chromatography (2.0 × 20 cm) with Silpearl UV silica gel. The chromatographically pure product was recrystallized from a mixture of hexane and acetone.

General Procedure for the Production of the Coumarins (X-XXVI). To a solution of 4.0 mmole of the initial coumarin (I-IX) in 10-20 ml of glacial acetic acid we added 4.0 mmole of the respective amine and 1.0 ml of 40% formalin. The mixture was stirred at 20-100°C for 5-20 h until the initial coumarin had disappeared (TLC). The acetic acid was distilled under vacuum, and the residue was treated with 20% aqueous sodium carbonate solution (15-25 ml) and extracted with methylene chloride (3 × 100 ml). The organic phase was evaporated, and the residue was separated by column chromatography with silica gel (2.0 × 20 cm) with hexane—acetone mixtures in ratios between 10:1 and 2:1 respectively as eluant. When required, the chromatographically pure product can be recrystallized from a mixture of hexane and acetone.

General Procedure for the Production of the Coumarins (XXVII, XXVIII). To a solution of 2.4 mmole of the coumarin (XIII) or the coumarin (XXI) in 20 ml of acetic acid we added 2.4 mmole of the coumarin (VII) and 1.0 ml of 40% formalin. The reaction mixture was stirred at 75°C for 1.5 h, the acetic acid was distilled under vacuum, and the residue was dissolved in 100 ml of methylene chloride and washed with water (3 × 50 ml). The organic phase was dried over calcined sodium sulfate, evaporated, and separated on a column (3.0 × 10.0 cm) of neutral aluminum oxide (5 × 40 μ) with a 2:1 mixture of hexane and methylene chloride as eluant. The chromatographically pure product was recrystallized from a mixture of acetone and methylene chloride.

General Procedure for the Production of the Salts (XXIX-XXXII). After distillation of the acetic acid from the reaction mixture obtained by the procedure described above the residue was dissolved in 10 ml of benzene and filtered. The filtrate was evaporated and separated by chromatography on a column of silica gel (2.0 × 20 cm) with a 4:1 mixture of hexane and acetone as eluant. The product was recrystallized from a mixture of hexane and acetone.

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