PHOTOCHEMICAL REACTIONS OF 7-AMINOCOUMARINS.

7.* REACTION OF 3-IODO-4-METHYL-7-DIETHYLCOUMARIN WITH OLEFINS

N. A. Gordeeva, M. A. Kirpichenok, D. S. Yufit,
Yu. T. Struchkov, and I. I. Grandberg

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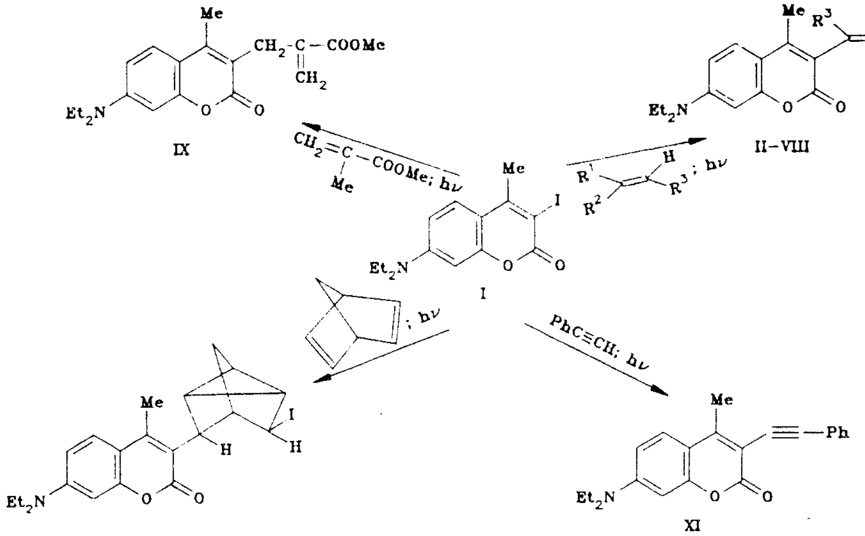
A number of new 7-aminocoumarins having an unsaturated substituent in the 3 position were obtained as a result of photolysis of 3-iodo-4-methyl-7-diethylaminocoumarin with olefins, viz., styrene, acrylonitrile, methyl acrylate, methyl methacrylate, 4-vinylpyridine, 2-ethoxypropene, indene, ethyl β-anilinocrotonate, and 2,5-norbornadiene, as well as with phenylacetylene. Regiospecificity and stereospecificity of the investigated photoreactions were established. The spectral-luminescence characteristics of the synthesized compounds are presented.

The possibility of the synthesis of diverse 3-substituted 7-aminocoumarins was demonstrated in [2] in the case of photoreactions of 4-methyl-7-diethylaminocoumarin with alkyl and aryl halides. It was established that reactions of this type proceed via a radical or ion-radical mechanism, are accelerated by triethylamine, and are realized most effectively for aryl iodides and activated alkyl bromides.



II—V, VII $R^1=H$, VI $R^1=OC_2H_5$, VIII $R^1=NHC_6H_5$; II $R^2=C_6H_5$, III $R^2=CN$, IV $R^2=COOCH_3$, V $R^2=4\text{-}C_5H_4N$, VI, VIII $R^2=CH_3$; II—VI $R^3=H$, VIII $R^3=COOC_2H_5$; VII $R^2+R^3=o\text{-}CH_2—C_6H_4$

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*For Communication 6, see [1].

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The photochemical reactions of 3-iodo-7-aminocoumarins with unsaturated compounds may serve as another method for the synthesis of 3-substituted 7-aminocoumarins. In this connection, in the present research we studied the photoreactions of 3-iodo-4-methyl-7-diethylaminocoumarin (I) with olefins with various structures, viz., styrene, acrylonitrile, methyl acrylate, methyl methacrylate, 4-vinylpyridine, 2-ethoxypropene, indene, ethyl β-anilinocrotonate, and 2,5-norbornadiene. For most of the olefins the principal products of the photoreactions were 3-alkenylcoumarins II-VIII. Methyl methacrylate and norbornadiene, in the reactions with which IX and X were obtained, constituted an exception.

4-Methyl-7-diethylaminocoumarin and products of N-de-ethylation of this compound [3] and the starting coumarin were detected as side substances in the reaction mixtures. In the course of the photolysis we also observed the accumulation of appreciable amounts of iodine. The use of various solvents (CH_3CN, DMSO, C_6H_6, dioxane, etc.) usually led to an increase in the percentage of 4-methyl-7-diethylaminocoumarin, an increase in the duration of the photoreactions, and, as a consequence, a decrease in the yields of coumarins II-X.

The structures of the synthesized compounds were established primarily from spectral data (Tables 1-3). The IR spectra of coumarins II-X contain an absorption band of a lactone C=O group at 1650-1710 cm^{-1}. Vibrations of C=C bonds are usually observed in the form of two intense bands at 1605-1620 cm^{-1}. Additional absorption bands of CN and C=O functional groups (Table 1) confirm retention of the structure of the substituent in coumarins III, IV, VIII, and IX.

Signals of "coumarinyl" 5-H, 6-H, and 8-H protons, which appear at 7.4-7.5, 6.6-6.7, and 6.4-6.6 ppm with characteristic spin-spin coupling constants (SSCC) [4], are readily identified in the PMR spectra of the investigated compounds (Table 2). The presence of a substituent in the 3 position is proved indirectly by the absence of a signal of a 3-H proton.

Alkenyl coumarins II-V are E isomers; this follows from the vicinal SSCC, which are equal to 15.6-17.5 Hz. The chemical shifts of the H_α and H_β olefinic protons in coumarins II-IV were also calculated via an additive scheme [5]. For the H_α protons the theoretical and experimental values coincide with an accuracy of up to 0.2 ppm, while for the H_β protons the actually observed values are shifted 0.6-1.0 ppm to weak field, which can be explained by the deshielding effect of the lactone carbonyl group. Proceeding from these data one may assume that the diene system formed by the $C_{(3)}=C_{(4)}$ bond and the olefin fragment of the substituent in II-V and VII has an s-trans configuration. To verify this assumption we conducted an x-ray diffraction study of coumarin IV, which confirmed our preliminary conclusion.

Similar calculations for coumarin VI showed that the most probable structure for this compound is that of the Z isomer, in which the less electron-donor substituent is trans-oriented relative to the coumarin residue. Since in the spectrum of VIII the resonance signal of the NH proton is observed at rather weak field (11.3 ppm), the existence of an intramolecular hydrogen bond in solution between the NH group and the carbonyl group of the lactone ring is possible; this is additionally confirmed by the shift to the low-frequency region of the band of carbonyl absorption in the IR spectrum of VIII. In VIII the protons of the OCH_2 group are diastereotopic and show up in the PMR spectrum in the form of a doublet of quartets ($^2J = 15.0$, $^3J = 7.0$ Hz). The nonequivalence of the methylene protons is in best agreement with an s-trans configuration of the $C_{(4)}=C_{(3)}-C_\alpha=C_\beta$ diene system, since in this case rotation about the OCH_2 bond should be hindered.

In the spectrum of coumarin IX the signals of the olefinic protons are observed in the form of a doublet of doublets with geminal SSCC $J = 1.5$ Hz and allylic constants $J = -1.3$ Hz and $J = -1.8$ Hz. The small value of the geminal SSCC is evidently explained by the presence in the β position relative to the olefinic protons of an electron-acceptor methoxycarbonyl group [5]. The assignment of the signals of the protons of the nortricyclene fragment in coumarin X was made in analogy with the known data for 3-monosubstituted and exo,exo- and exo,endo-3,5-disubstituted nortricyclenes [6] and indicates an exo,exo configuration of the substituents in X. Of no small significance also is the fact that yet another nortricyclene isomer was detected in trace amounts on the reaction mixture; to this isomer we assigned a structure with an exo orientation of the coumarinyl substituent and an endo orientation of the iodine atom, since the weak-field shift of the signals of 5-H protons observed in the PMR spectrum of this compound usually occurs with a change in the configuration of the halogen atom [6].

The absorption spectra of II-VIII (Table 3) confirm the existence of an additional conjugation chain due to the introduction of an alkenyl substituent. Characteristic absorption maxima in ethanol and acetonitrile are observed at 240-255, 280-300, 305-330, and 370-440 nm. The long-wave absorption maximum in the spectra of coumarins II-VIII undergoes a bathochromic shift with an increase in the electron-acceptor properties of the substituents attached to the double bond. The UV spectra of coumarins IX and X are similar to the spectra of other 3-alkylcoumarins [2, 7]. Coumarins II-X have luminescence at 450-520 nm (Table 3); II, IV, VI, IX, and X fluoresce most intensely ($\varphi_f > 0.5$). In contrast to the long-wave absorption band, the emission band does not display any distinct dependence on the electronic character of the 3-alkenyl substituent. Evidence for this is also provided by the rather markedly changed values of the Stokesian shifts – from 32 nm for coumarin V to 128 nm for coumarin VII in ethanol. The fact of retention of intense luminescence properties in iodo derivative X, in which the quenching effect of the heavy atom is evidently blocked by the carcass skeleton of the substituent, is interesting.

TABLE 1. Characteristics of the Synthesized Compounds*

Compound	Empirical formula	mp, °C	R_f (system)**	IR spectrum, ν, cm^{-1}		φ***	Reaction time, h	Conversion, %	Yield, %
				C=O	C=C				
II	$C_{22}H_{23}NO_2$	149	0,49 (A)	1695	1610	0,0510	10	100	43
III	$C_{17}H_{18}N_2O_2$	187	0,24 (B)	1700, 2300 (C≡N)	1610	0,004	18	50	21
IV	$C_{18}H_{21}NO_4$	184...185	0,17 (A)	1715, 1695	1615	0,0005	18	45	30
V	$C_{21}H_{22}N_2O_2$	210 (dec.)	0,40 (C)	1700	1610	0,0010	20	55	20
VI	$C_{19}H_{25}NO_3$	90	0,08 (A)	1700	1610	0,0170	12	90	31
VII	$C_{23}H_{23}NO_2$	145	0,39 (B)	1700	1605	—	15	80	23
VIII	$C_{26}H_{30}N_2O_4$	67	0,36 (D)	1715, 1650	1620	—	15	95	28
IX	$C_{19}H_{23}NO_4$	84	0,16 (A)	1710, 1690	1605	—	15	90	31
X	$C_{21}H_{24}INO_2$	158...159	0,17 (E)	1700	1620	—	15	50	24
XI	$C_{22}H_{21}NO_2$	145	0,29 (B)	1705	1605	0,0150	14	100	30

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*For VIII, M$^+$ 434; for IX, M$^+$ 449.

**System A is benzene–acetone (20:1), system B is hexane–acetone (3:1), system C is hexane–acetone (1:1), system D is hexane–ether (1:1), and system E is benzene.

***φ is the quantum yield of the reaction.

TABLE 2. PMR Spectra of II-XI

Compound	Chemical shifts, δ, ppm (in $CDCl_3$) (SSCC, J, Hz)						
	5-H, d ($J=9,0$)	6-H, dd ($J=9,0$, $J_1=2,5$)	8-H, d ($J=2,5$)	4-CH$_3$, s	NCH$_2$, q ($J=7,0$)	CH$_3$, t ($J=7,0$)	other protons
II	7,45	6,59	6,47	2,49	3,39	1,20	7,14 (1H, d, $J=17,5$, H_α); 7,10...7,60 (5H, m, C_6H_5); 7,63 (1H, d, $J=17,5$, H_β)
III	7,51	6,64	6,46	2,48	3,43	1,22	6,84 (1H, d, 16,0, H_β); 7,43 (1H, d $J=16,0$; H_α)
IV	7,51	6,62	6,47	2,52	3,43	1,22	3,78 (3H, s, OCH_3); 7,18 (1H, d $J=15,6$; H_β), 7,52 (1H, d $J=15,6$, H_α)
V	7,50	6,62	6,48	2,52	3,40	1,20	7,36 (1H, d, $J=16,0$; H_β); 7,64 (2H, m, H_{arom}; 7,68 (1H, d $J=16,0$; H_α); 8,53 (2H, m, H_{arom})
VI	7,41	6,63	6,52	2,28	3,40	1,19	1,22 (3H, t, $J=7,0$, CH_3); 2,24 (3H, s =C—CH_3); 3,72 (2H, q $J=7,0$, OCH_2); 3,75 (1H, s H_α)
VII	7,44	6,63	6,53	2,50	3,40	1,20	3,84 (2H, s, CH_2); 6,78 (1H, s, =CH); 7,12...7,42 (4H, m, C_6H_4)
VIII	7,45	6,63	6,56	2,28	3,40	1,20	1,15 (3H, t 7,0, CH_3); 1,85 (3H, s, =C CH_3); 4,09 (1H, dq, $J=15,0$; $J=7,0$, CH); 4,10 (1H, dq, $J=15,0$; $J=7,0$, =CH); 7,05...7,35 (5H, m, C_6H_5), 11,3 (1H, s NH)
IX	7,45	6,68	6,57	2,31	3,42	1,20	3,64 (2H, dd $J=-1,3$, $J=-1,8$, CH_2); 3,77 (3H, s, OCH_3); 5,43 (1H, dd, $J=1,5$, $J=-1,8$, CH_2—C=CH_{trans}); 6,22 (1H, dd $J=1,5$, $J=-1,3$, CH_2—C=CH_{cis})
X	7,43	6,59	6,46	2,50	3,39	1,18	$\left.\begin{matrix}1{,}30\ldots1{,}70\ (4H,\ m)\\2{,}07\ (1H,\ d.)\end{matrix}\right\}$ 1′-H, 2′-H, 6′-H, 7′-H; 2,36 (1H, s 4′-H); 3,09 (1H, t, $J=1,5$, 5′-H), 4,11 (1H, t $J=1,5$, 3′-H)
XI	7,42	6,80	6,47	2,60	3,40	1,20	7,30...7,60 (5H, m, C_6H_5)

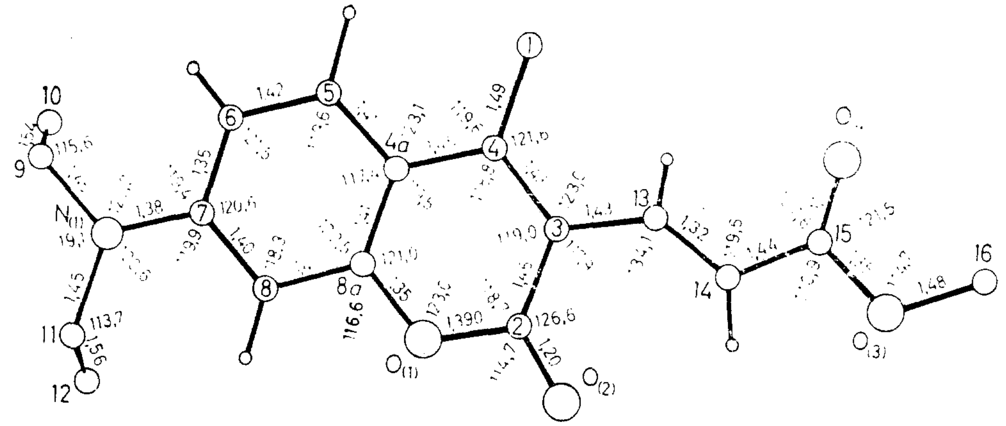
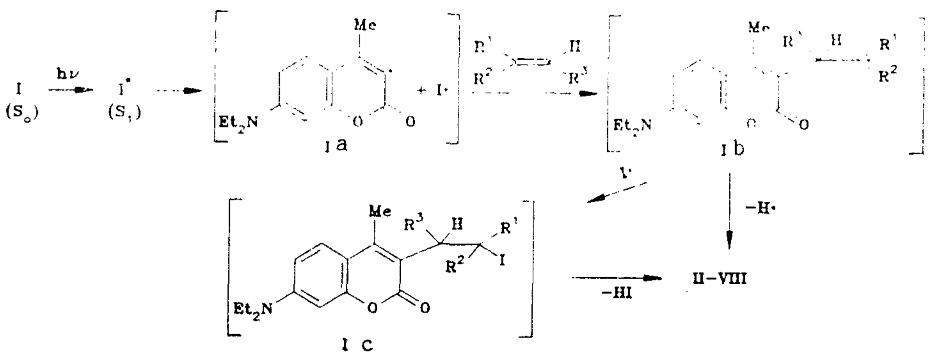


Fig. 1. Structure of the IV molecule in the crystal.

In order to unequivocally determine the conformation of the coumarin IV molecule, we conducted an x-ray diffraction study of this compound. In the crystal the IV molecule (with the exception of the CH_3, $C_{(10)}$, and $C_{(12)}$ groups) is planar (Fig. 1); this suggests participation of the methoxycarbonylvinyl substituent and the unshared pair of the nitrogen atom in conjugation with the π system of the benzopyran ring of the molecule. The lengthening of the $C_{(3)}$–$C_{(4)}$ bond to 1.43 Å in IV as compared with 1.32 Å in 3-unsubstituted 4-methyl-7-diethylaminocoumarin [8] is evidently due to the above-indicated conjugation with participation of the methoxycarbonylvinyl group. The IV molecule has a trans configuration relative to the $C_{(13)}$–$C_{(14)}$ bond, an s-trans configuration relative to the $C_{(3)}$–$C_{(13)}$ bond, and an s-cis configuration relative to the $C_{(14)}$–$C_{(15)}$ bond. The maximum deviation from 180° of the absolute values of the torsion angles is 6° (for $C_{(13)}C_{(14)}C_{(15)}O_{(3)}$) in the $C_{(3)}$-$C_{(16)}$ chain. The planar conformation of the side chain of the IV molecule leads to the development in it of a number of short intramolecular $C_{(1)}...C_{(13)}$ (2.99 Å), $O_{(2)}...C_{(14)}$ (2.88 Å) and $C_{(13)}...O_{(4)}$ (2.83 Å) contacts, which give rise, in turn, to an appreciable increase in the $C_{(3)}C_{(13)}C_{(14)}$ [134.1(9)°], $C_{(14)}C_{(15)}O_4$ [127.6(9)°], and $C_{(4)}C_{(3)}C_{13)}$ [123.0(8)°] bond angles.

In order to evaluate the possible areas of application of the investigated photoreactions we also studied the reaction of coumarin I with phenylacetylene, which leads to the formation of coumarin XI.



The most probable mechanism for the "photohetarylation" reactions under consideration is a radical mechanism with the participation of 3-coumarinyl radical Ia, which may be formed from the excited S_1 state of coumarin I. It is known that similar processes are realized for most aryl iodides [9]. The subsequent addition of a coumarinyl radical to the multiple bond should lead to radical Ib, which is converted to the desired product after the elimination of a hydrogen atom or through a step involving the corresponding iodo derivative Ic.

The occurrence of the investigated reactions with olefins that differ with respect to their electronic properties the accumulation of iodine in the reaction mixtures, and the quenching of the photoreactions by polyhalomethanes (CCl_4, $CHCl_3$) and hydrogen donors (alkanes, ethers, etc.) constitute evidence in favor of a radical mechanism. Within the framework of a radical mechanism one can understand the formation of coumarin IX, which can be obtained from a radical of the Ib type as a result of detachment of a hydrogen atom from the β-CH_3 group. Another pathway that includes radical attack in the allylic position seems less likely, since it should contain a step involving recombination of two radicals. The absence of analogous products in the case of coumarins VI and VIII is possibly explained by the effective realization of a step involving the addition of an I· particle to the "nucleophilic" radical center of the Ib type in such a way that the reaction subsequently is ionic elimination leading to retention of the conjugation chain.

The formation of rearrangement products of the X type in radical reactions of norbornadiene is also well known [6].

TABLE 3. Spectral-Luminescence Properties of II-XI

Compound	Solvent	UV spectrum, λ_{max}, nm (log ε)	λ		Luminescence	
			excit.	max.	Stokesian shift, nm	φ_f
II	C_2H_5OH	244 (4,30), 286 (4,19), 290 (4,22), 414 (4,76)	400	490	76	0,61
	CH_3CN	241 (4,31), 286 (4,14), 296 (4,16), 414 (4,72)	400	490	76	0,71
III	C_2H_5OH	251 (4,09), 278 (4,09), 297 (4,00), 328 (3,57), 440 (4,82)	440	494	54	0,19
	CH_3CN	251 (4,03), 278 (4,07), 294 (3,94), 436 (4,70), 436 (4,70)	440	492	56	0,20
IV	C_2H_5OH	253 (4,07), 280 (4,06), 297 (3,97), 329 (3,62), 436 (4,71)	430	494	58	1,00
	CH_3CN	252 (3,95), 278 (3,96), 296 (3,86), 328 (3,56), 430 (4,62)	430	490	60	0,80
V	C_2H_5OH	224 (4,30), 287 (3,97), 304 (3,99), 428 (4,63)	400	460	32	0,46
	CH_3CN	287 (3,97), 304 (3,91), 423 (4,66)	400	450	27	0,22
VI	C_2H_5OH	246 (4,18), 260 (4,20), 308 (3,70), 385 (4,46)	375	475	90	0,60
	CH_3CN	241 (4,17), 258 (4,14), 306 (3,69), 320 (3,80), 375 (4,49)	375	465	90	0,52
VII	C_2H_5OH	246 (4,33), 280 (4,04), 308 (3,86), 392 (4,58)	390	520	128	<0,1
	CH_3CN	245 (4,17), 280 (3,83), 310 (3,66), 386 (4,42)	390	520	134	<0,1
VIII	C_2H_5OH	250 (4,30), 307 (4,40), 384 (4,47)	375	464	80	<0,1
	CH_3CN	247 (4,25), 306 (4,36), 376 (4,45)	375	460	84	<0.1
IX	C_2H_5OH	248 (4,20), 254 (4,18), 308 (3,54), 318 (3,61), 369 (4,41)	375	462	93	0,64
	CH_3CN	245 (4,17), 254 (4,12), 306 (3,61), 318 (3,72), 373 (4,40)	375	450	77	0,59
X	C_2H_5OH	220 (4,61), 253 (4,28), 310 (3,72), 320 (3,76), 380 (4,43)	375	464	84	0,61
	CH_3CN	249 (4,18), 310 (3,67), 320 (3,69), 372 (4,44)	374	448	76	0,34
XI	C_2H_5OH	239 (4,18), 260 (4,11), 278 (4,14), 290 (4,13), 312 (3,84), 326 (3,67), 420 (4,68)	400	480	60	0,80
	CH_3CN	236 (4,23), 258 (4,14), 278 (4,14), 290 (4,10), 312 (3,81), 326 (3,67), 417 (4,69)	400	477	60	0,73

TABLE 4. Coordinates of the Atoms ($\cdot 10^4$; $\cdot 10^3$ for the H atoms) of the IV Molecule

Atom	x	y	z
$O_{(1)}$	178(12)	2009	7239(8)
$O_{(2)}$	2889(13)	1654(3)	5414(8)
$O_{(3)}$	8795(14)	4(3)	4656(9)
$O_{(4)}$	8530(14)	−299(3)	7490(10)
$N_{(1)}$	−5985(14)	2903(3)	10820(9)
$C_{(1)}$	2293(20)	579(4)	11160(13)
$C_{(2)}$	2058(17)	1578(4)	6839(11)
$C_{(3)}$	2855(17)	1096(4)	8157(12)
$C_{(4)}$	1633(17)	1073(4)	9790(13)
$C_{(4a)}$	−340(16)	1533(4)	10089(13)
$C_{(5)}$	−1680(17)	1545(4)	11641(12)
$C_{(6)}$	−3557(18)	2017(4)	11845(11)
$C_{(7)}$	−4147(16)	2451(4)	10558(11)
$C_{(8)}$	−2848(18)	2458(4)	8993(11)
$C_{(8a)}$	−992(17)	1994(4)	8777(11)
$C_{(9)}$	−7086(21)	2946(5)	12544(15)
$C_{(10)}$	−5225(25)	3235(6)	14119(13)
$C_{(11)}$	−6699(18)	3365(5)	9446(14)
$C_{(12)}$	−4707(22)	3919(5)	9540(15)
$C_{(13)}$	4776(18)	656(4)	7718(12)
$C_{(14)}$	6058(16)	566(4)	6301(11)
$C_{(15)}$	7884(19)	56(4)	6290(15)
$C_{(16)}$	10658(21)	−516(4)	4507(16)
$H_{(5)}$	−146(15)	117(4)	1262(10)
$H_{(6)}$	−430(16)	201(4)	1287(11)
$H_{(8)}$	−312(16)	281(3)	811(11)
$H_{(9.1)}$	−806(16)	256(4)	1270(11)
$H_{(9.2)}$	−889(15)	328(4)	1202(10)
$H_{(11.1)}$	−817(16)	351(4)	970(11)
$H_{(11.2)}$	−641(14)	327(4)	835(11)
$H_{(13)}$	562(15)	50(4)	876(11)
$H_{(14)}$	591(15)	73(4)	514(12)

For a more detailed understanding of the mechanism of the investigated processes we also measured the quantum yields of reactions involving the formation of coumarins II-VI and XI (Table 1). It was found that the effectiveness of photosubstitution decreases by more than an order of magnitude with an increase in the electron-acceptor properties of the substituent in the olefin. This fact, in principle, indicates the electrophilic character of the 3-coumarinyl radical, which evidently should be regarded as a σ radical [10] that has electrophilic properties as a result of the electron-acceptor effect of the α-carbonyl group. It might be assumed that the regiospecificity of the reactions under consideration is determined by the stability of a radical of the Ib type, while the stereospecificity is dictated by the thermodynamic stability of the final product, in which a condition of the best conjugation of the 7-aminocoumarin fragment and the β substituent in the olefin is their mutual trans orientation.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a Perkin–Elmer 577 spectrometer. The UV spectra and the luminescence spectra were obtained with an EPS-3T spectrophotometer with a G3 luminescence adapter. The relative luminescence quantum yields were determined with respect to 3-aminophthalimide [11]. The PMR spectra of solutions in $CDCl_3$ were obtained with a Bruker WM spectrometer (250 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The mass spectra were obtained with a Varian MAT-311A mass spectrometer (ionizing voltage 70 eV). The reaction products were isolated by chromatography with columns (40 × 3.5 cm) packed with Silpearl UV-254 as the sorbent in hexane–acetone, benzene–acetone, and hexane–ether systems. Monitoring of the purity of the substances was accomplished by means of TLC on Silufol plates with development by UV light and with iodine. The conversion was determined with respect to the residual I after column chromatography of the reaction mass. The differential quantum yields were calculated by the method in [10] and were determined for solutions of coumarin I (0.05 mole/liter) in the corresponding unsaturated compounds in the case of irradiation of them with light with a wavelength of 370 nm obtained by means of a Shimadzu NGF-16 monochromator. The intensity of the source I_0 determined by the standard method [10] was $3.72 \cdot 10^{-10}$ ergs/sec. The quantitative evaluation of the reaction products formed was carried out by means of a Shimadzu CS-930 densitometer after separation of the reaction masses on Kieselgel 60 plates (Merck). The results of elementary analysis for C, H, and N were in agreement with the calculated values.

General Method for Obtaining Coumarins II-XI. A solution of 1 g (3 mmoles) of coumarin I in 100 ml of the corresponding unsaturated compound was irradiated with the light of a PRK-2 medium-pressure mercury lamp in a 100-ml glass reactor with stirring with a stream of nitrogen for 10-20 h. The reaction mass was evaporated, the residue was separated by column chromatography [elution with benzene for II, IV, IX, and X, with hexane–acetone (10:1) for III, VII, and XI, with hexane–acetone (5:1) for V, with benzene–acetone (30:1) for VI, and with hexane–ether (4:1) for VIII], and the isolated products were crystallized from hexane–acetone.

X-Ray Diffraction Study of IV. The crystals of IV ($C_{18}H_{21}NO_4$) were monoclinic and had the following parameters at 20°C: $a = 5.030(1)$, $b = 21.774(4)$, $c = 7.430(1)$ Å, $\beta = 97.12(1)°$, $Z = 2$, $d_{calc} = 1.20$ g/cm^3. space group $P2_1$. The cell parameters and the intensities of 1067 reflections, 593 of which with $I \geq 2\sigma(I)$, were used in decoding and refining the structure and were measured with a Hilger–Watts automatic diffractometer ($\lambda_{Mo K_\alpha}$, graphite monochromator, $\theta/2\theta$ scanning $\theta \leq 26°$). The structure was decoded by the direct method and was refined by the total-matrix method of least squares within the anisotropic approximation for all of the nonhydrogen atoms. As a consequence of the small number of reflections obtained, which is associated with the low quality of the crystal, the hydrogen atoms of the CH_3 groups could not be revealed. The remaining hydrogen atoms were placed in the calculated positions and refined with fixed $B_{iso} = 6$ Å^2. The final divergence factors $R = 0.058$ and $R_w = 0.053$. All of the calculations were made with an Eclipse S/200 computer by means of INEXTL programs [12]. The coordinates of the atoms are presented in Table 4.

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