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CONVERSIONS OF COUMARINS ACCOMPANIED BY INTERMEDIATE OPENING AND RECYCLIZATION OF THE LACTONE RING. 2*. STUDY OF THE INTERACTION OF MALONIC ACID HYDRAZIDE AND AMIDE DERIVATIVES WITH 3-ACYL(3-CYANO, 3-ETHOXYCARBONYL)COUMARINS

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Reaction between the N,N'-diisopropylidene and N,N'-diacetyl derivatives of malonic acid dihydrazide and 3-acyl(3-cyano, 3-ethoxycarbonyl)coumarins under the conditions of the Michael reaction lead to the formation of N'-isopropylidene and N'-acetyl derivatives of coumarin-3-carboxylic acid hydrazide. Ethoxycarbonylacethydrazide reacts in an analogous manner. Special features have been studied of the interaction of malonic acid amide derivatives with unsubstituted coumarin and with coumarins containing electron-withdrawing groupings in position 3 of the ring.

Keywords: 3-acyl(3-cyano, 3-ethoxycarbonyl)coumarins, malonic acid hydrazide and amide derivatives, mass spectrometric study of reaction products and reaction mixtures, opening and recyclization of the coumarin lactone ring, Michael reaction.

Study of the interaction of 3-acyl(ethoxycarbonyl)coumarins with malonic acid dihydrazide under the conditions of the Michael reaction has shown that this reaction occurs analogously to the conversion of 3-acyl(ethoxycarbonyl)coumarins into 3-cyanocoumarins discovered by us previously [2, 3] with the formation of coumarin-3-carboxylic acid hydrazide **2**.

The resulting hydrazide **2**, in its turn, interacts with the initial 3-acyl(ethoxycarbonyl)coumarins with the formation of salicylidene derivatives of coumarin-3-carboxylic acid hydrazides **4**. The composition of the products essentially depends on the structure of the initial coumarin. In the case of coumarins unsubstituted in the benzene ring, and also their 6-methyl (6-Br) or 8-OMe derivatives, the salicylidene derivatives of coumarin-3-carboxylic acid hydrazides **4a-d** predominate among the reaction products [4]. In the case of 3-ethoxycarbonyl(acetyl)coumarins the formation of the corresponding N,N'-biscoumarinoyl-2-hydrazines **3a-c** was noted. These compounds are formed in insignificant amount and were not isolated in the pure state. Their presence in the reaction mixture was established by the presence in the mass spectra of the corresponding peaks for the molecular ions.

* For Part 1 see [1].

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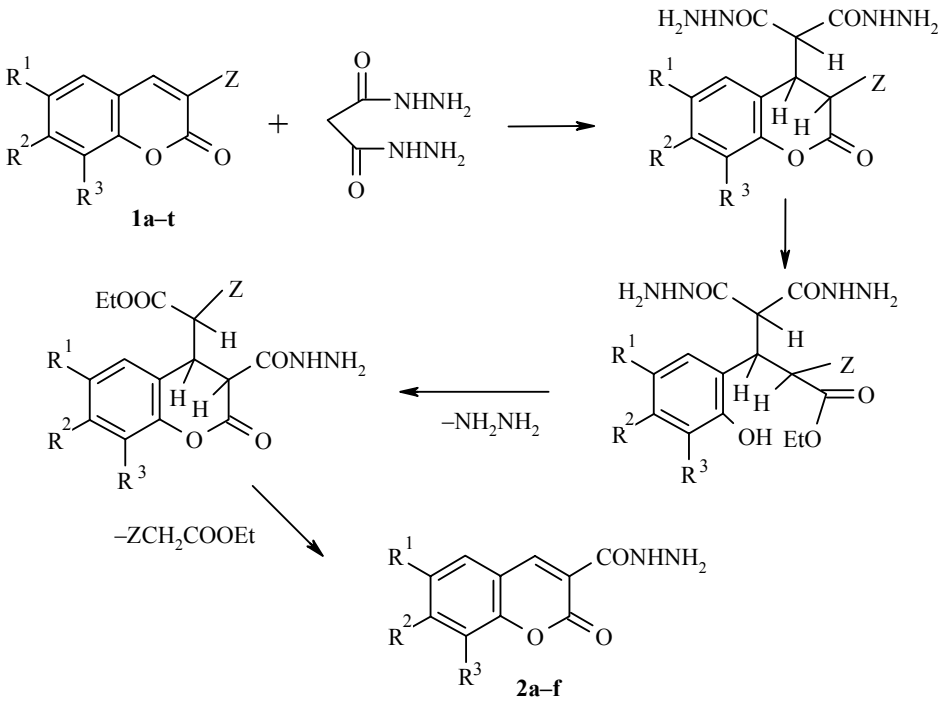
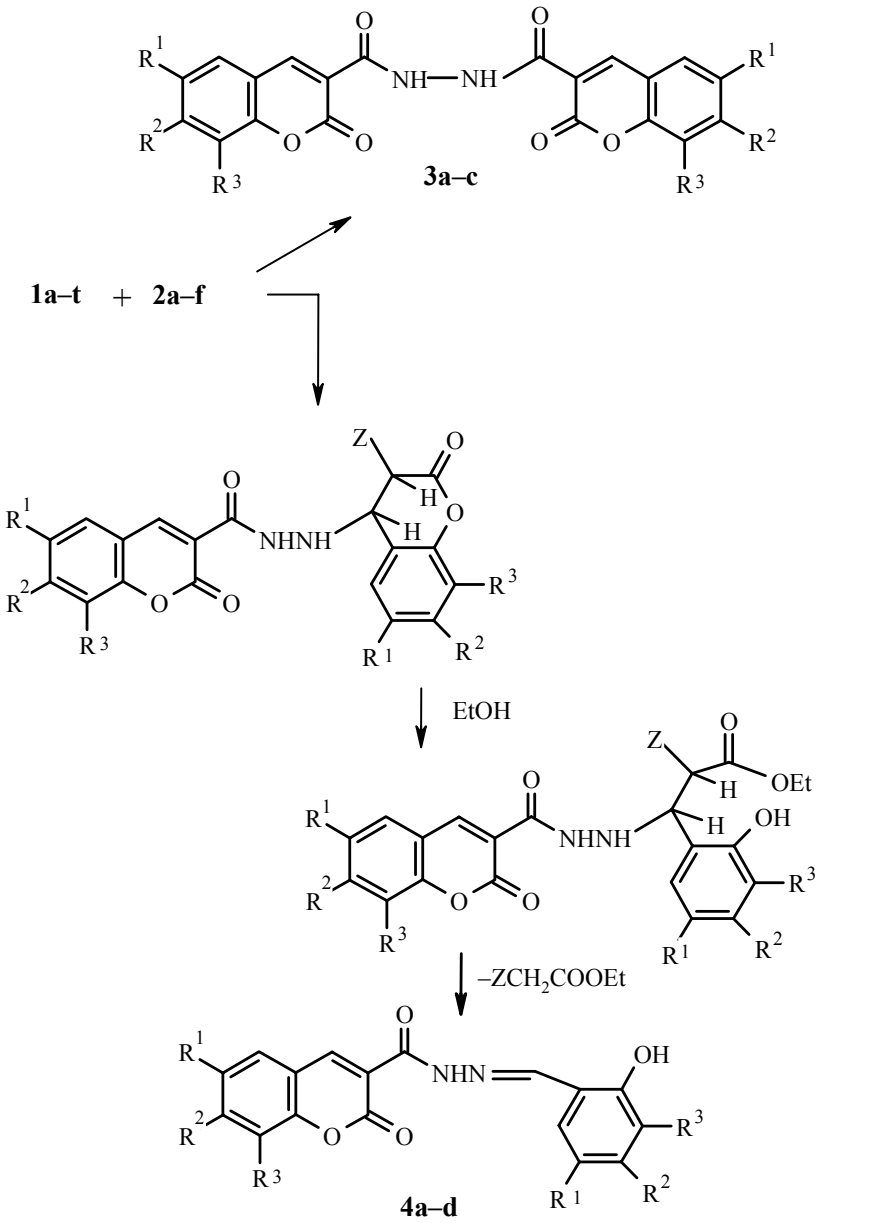


1 a Z = COOEt, $R^1 = R^2 = R^3 = H$; **b** Z = COMe, $R^1 = R^2 = R^3 = H$; **c** Z = COPh, $R^1 = R^2 = R^3 = H$; **d** Z = CN, $R^1 = R^2 = R^3 = H$; **e** Z = COOEt, R^1 = Me, $R^2 = R^3 = H$; **f** Z = COMe, R^1 = Me, $R^2 = R^3 = H$; **g** Z = COPh, R^1 = Me, $R^2 = R^3 = H$; **h** Z = COOEt, R^1 = OMe, $R^2 = R^3$ = H; **i** Z = CN, R^1 = OMe, $R^2 = R^3 = H$; **j** Z = COOEt, R^2 = Me, $R^1 = R^3 = H$; **k** Z = COMe, R^2 = Me, $R^1 = R^3 = H$; **l** Z = COPh, R^2 = Me, $R^1 = R^3$= H; **m** Z = CN, R^2 = OMe, $R^1 = R^3 = H$; **n** Z = COOEt, R^3 = OMe, $R^1 = R^2 = H$; **o** Z = COMe, R^3 = OMe, $R^1 = R^2 = H$; **p** Z = COPh, R^3 = OMe, $R^1 = H$; **q** Z = CN, R^3 = OMe, $R^1 = R^2 = H$; **r** Z = COOEt, R^1 = Br, $R^2 = R^3 = H$; **s** Z = COMe, R^1 = Br, $R^2 = R^3 = H$; **t** Z = COPh, R^1 = Br, $R^2 = R^3 = H$; **2 a** $R^1 = R^2 = R^3 = H$; **b** R^1 = Me, $R^2 = R^3 = H$; **c** R^1 = OMe, $R^2 = R^3 = H$; **d** $R^1 = R^3 = H$, R^2 = OMe; **e** $R^1 = R^2 = H$, R^3 = OMe,; **f** R^1 = Br, $R^2 = R^3 = H$

The reaction mixtures formed when using 6(7)-OMe-substituted coumarins contain significant amounts of coumarin-3-carboxylic acid hydrazides. When using 6(7)-OMe-substituted 3-cyano- and 3-acetylcoumarins the corresponding coumarin-3-carboxylic acid hydrazides were isolated as their isopropylidene derivatives **5a,b** by treating the reaction mixture with acetone.

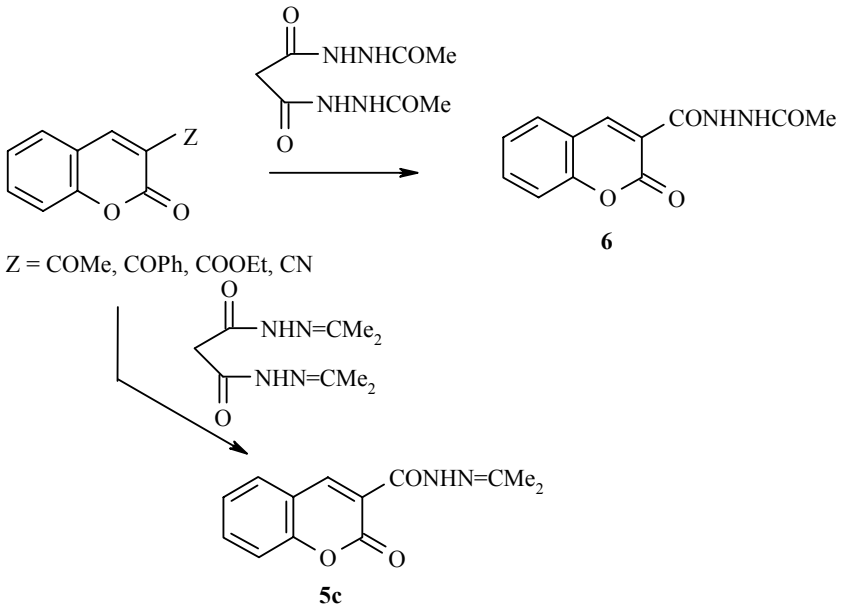
The use of diisopropylidene and diacetyl derivatives of malonic acid dihydrazide in reactions with 3-acyl(3-cyano, 3-ethoxycarbonyl)coumarins unsubstituted in the benzene ring ($R^1 = R^2 = R^3 = H$) enabled suppression of the formation of secondary conversion products of coumarin-3-carboxylic acid hydrazide. As a result N'-isopropylidene (**5c**) and N'-acetyl derivatives **6** of this compound were obtained in 70-80% yield.

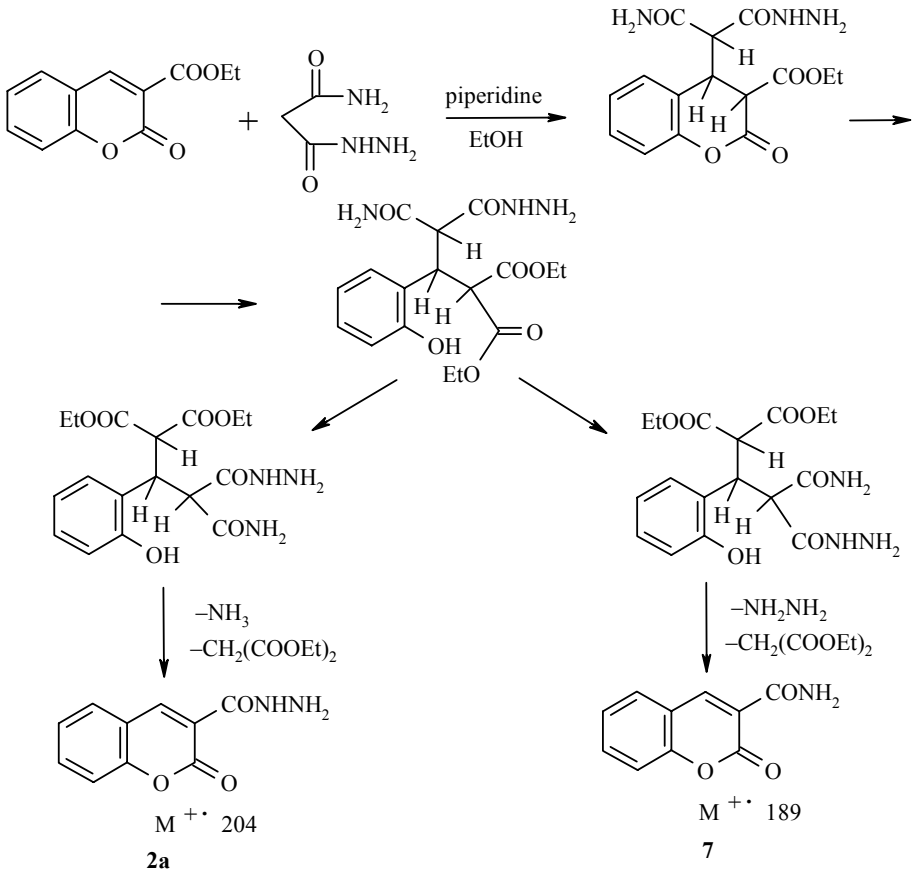
Data of mass spectrometry showed that in the synthesis of compound **5** the formation occurs of insignificant amounts of the salicylidene derivative of coumarin-3-carboxylic acid hydrazide. This is probably linked with partial hydrolytic elimination of the isopropylidene grouping in compound **5**. In the case of compound **6** this process was not observed. The composition and structure of compounds **5** and **6** were demonstrated by data of elemental analysis and also mass spectrometry. In the mass spectrum of compound **5** peaks were observed for $[M]^{+\cdot}$ 244, $[M\text{-Me}]^+$ 229, $[M\text{-NHN=CMe}_2]^+$ 173, and in the case of **6** $[M]^{+\cdot}$ 246, $[M\text{-COMe}]^+$ 204, and $[M\text{-NHNHCOMe}]^+$ 173.



3 a R^1 = Br, R^2 = R^3 = H; **b** R^1 = OMe, R^2 = R^3 = H; **c** R^2 = OMe, R^1 = R^3 = H;
4 a R^1 = R^2 = R^3 = H; **b** R^1 = Me, R^2 = R^3 = H; **c** R^1 = Br, R^2 = R^3 = H; **d** R^3 = OMe, R^1 = R^2 = H

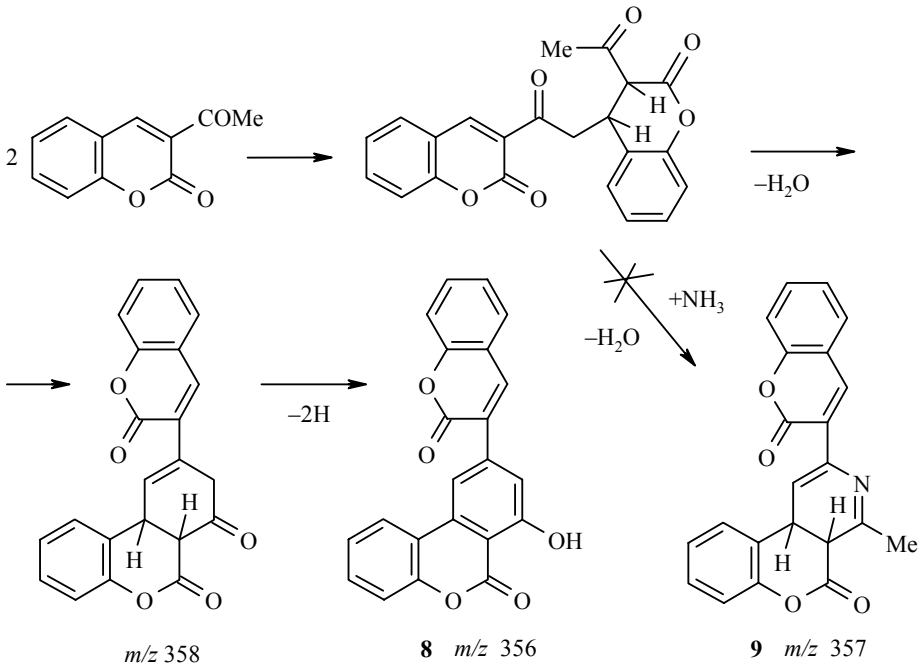
In the light of the data obtained it seemed of interest to clarify the behavior in this reaction of the hydrazide of malonic acid monoamide and its diamide. In the first case the interaction with 3-ethoxycarbonylcoumarin takes place at room temperature and leads to the formation of coumarin-3-carboxylic acid amide **7** in a yield of over 70%. Coumarin-3-carboxylic acid hydrazide **8** was present in the reaction mixture in minor amounts, which was established by mass spectrometry. The formation of coumarin-3-carboxylic acid amide probably proceeds by the same route as takes place on interaction of coumarins with malonic acid hydrazides. In this, opening of the lactone ring occurs in the initially formed product of the addition of malonic acid monoamide hydrazide at position 4 of the starting coumarin. Subsequent recyclization accompanied by a retro Michael reaction may theoretically take place with cleavage of both hydrazine and ammonia and thereby lead to the formation of hydrazide **2a** or coumarin-3-carboxylic acid amide **7**.





On the basis that amide **7** predominates even at room temperature in the reaction products, it may be concluded that the more preferred direction for recyclization of the intermediate product of coumarin lactone ring opening is cleavage of hydrazine and not ammonia.

The interaction of 3-acyl (3-cyano, 3-ethoxycarbonyl)coumarins with malonic acid diamide proceeds under far more drastic conditions. To carry out this process boiling the reaction mixture (in ethanol) for a minimum of 6 h is required, which leads in the final count to the formation in all cases of the same compound, coumarin-3-carboxylic acid amide **7**. In the case of 3-acetylcoumarin the formation of minor amounts of a compound with *m/z* 356 was recorded in the reaction mixture by mass spectrometry, and was assigned the tricyclic structure **8***. The formation of this substance may be explained by condensation of two molecules of the initial 3-acetylcoumarin according to the Michael reaction with subsequent closure of the third ring.



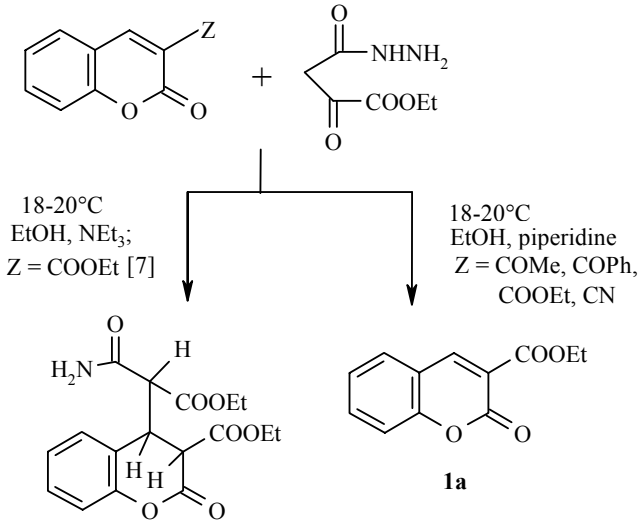
m/z 358 **8** *m/z* 356 **9** *m/z* 357

It should be mentioned that compound **9** with *m/z* 357 was not detected in the reaction products. The formation of **9** might have been expected from the data of [6]. According to [6] under the conditions of the Michael condensation the nitrogen-containing methylene component (malondiamide in this case) may be decomposed with liberation of ammonia. Previously the formation of compound **9** was recorded on interacting 3-acetylcoumarin with cyanoacetamide and β-aminocrotonic acid ester [6, 7]. It is evident that in our case malonic acid diamide does not play the role of ammonia donor.

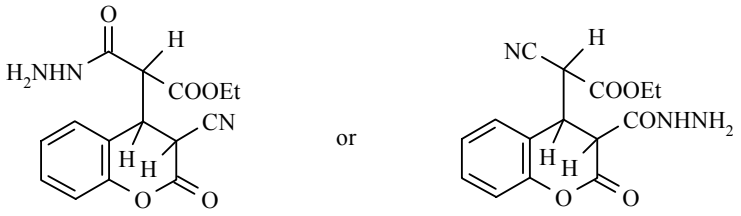
The somewhat contradictory picture is not clarified by adding in the results of the reaction of nitrogen-containing malonic acid derivatives with 3-substituted coumarins [4, 6, 7]. According to these data, unlike malondiamide, on interacting such derivatives as ethyl malonate monoamide and cyanoacetamide with 3-Z-substituted coumarins (Z = CN, COMe, COPh, COOEt) in the presence of bases, the process stops at the stage of forming the addition product at position 4 of the initial coumarin [7, 8], though in the latter case [8] the conditions of carrying out the reaction were completely analogous to those used by us when studying the interaction of malondiamide with 3-substituted coumarins. Opening of the lactone ring of the coumarin was not observed either in the case of the reaction of 3-acetylcoumarin with cyanoacetamide and its thio analog under the conditions indicated above. The reaction products were derivatives of benzopyrano[3.4-*c*]pyridine analogous to compound **9** mentioned previously in [5].

* The process of aromatization of tricyclic derivatives of coumarin by dehydrogenation was reported in [5].

Because of these data the interaction was studied of ethyl malonate monohydrazide with 3-Z-substituted coumarins (Z = CN, COMe, COPh, COOEt) under conditions analogous to those described in [7], where on interacting ethyl malonate monoamide with 3-ethoxycarbonylcoumarin only the Michael reaction adduct was isolated. However we were unsuccessful in isolating the Michael adduct from the reaction mixture, since the reaction proceeded through opening of the coumarin lactone ring with subsequent recyclization and led practically to one product, 3-ethoxycarbonylcoumarin, which corresponds completely to the process observed in the case of forming 3-cyanocoumarins [2] and derivatives of coumarin-3-carboxylic acid hydrazide [4].

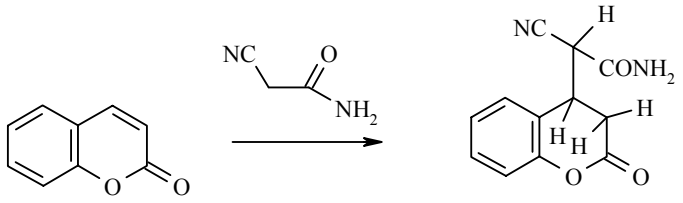


Analysis of the composition of reaction mixtures formed in each actual case (Z = COMe, COPh, COOEt*, CN) enabled confirmation of the course of the conversion being studied. For Z = COOEt, together with the initial coumarin and the final product **1a** (*m/z* 218), the presence was established in the reaction mixture of coumarin-3-carboxylic acid hydrazide (*m/z* 204), bis-N,N'-(3-coumarinoyl)hydrazine (*m/z* 376), pyrazolidine-3,5-dione (*m/z* 100), and the N'-ethoxymalonylhydrazide of coumarin-3-carboxylic acid (*m/z* 318). When Z = COMe, together with the final product **1a** (*m/z* 218), the presence was established of coumarin-3-carboxylic acid hydrazide (*m/z* 204), 3-methylpyrazolone (*m/z* 98), N'-ethoxymalonylhydrazide of coumarin-3-carboxylic acid (*m/z* 318), bis-N,N'-(3-coumarinoyl)hydrazine (*m/z* 376), and compounds with $[M]^{+\cdot}$ 348 and 346 with structures possibly corresponding to the Michael adduct (with addition of acetoacetic ester at position 4 of 3-ethoxycarbonyl-coumarin and the product of its aromatization at the 3-4 bond). When using 3-benzoylcoumarin as starting material, apart from the final product **1a** (*m/z* 218), coumarin-3-carboxylic acid hydrazide (*m/z* 204) and 3-phenylpyrazol-5-one (*m/z* 160) were detected in the reaction mixture. Finally, in the reaction with 3-cyanocoumarin, peaks were observed in the reaction mixture for molecular ions with *m/z* 218 (**1a**), 204 (coumarin-3-carboxylic acid hydrazide), and a low-intensity peak with *m/z* 317, which may be attributed to one of two structures.



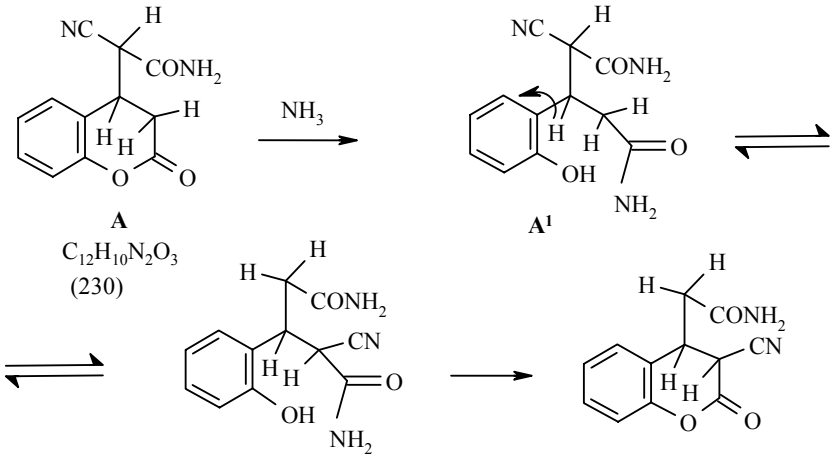
* When Z = COOEt in the initial coumarin the structure of the final product is identical to the initial structure.

The data under consideration belong to a coumarin derivative containing an electron-withdrawing substituent at position 3 of the ring. However it is known that many reactions proceeding readily with such coumarins, do not go with compounds in which substitution at position 3 is either absent or has an electron-donating character [8, 9]. Starting from this it seemed of interest to us to clarify the character of the interaction of cyanoacetylhydrazine and its N-isopropylidene derivative with unsubstituted coumarin under conditions analogous to those used in the reaction of 3-substituted coumarins. The interaction of coumarins with the simplest analog of cyanoacetylhydrazine, cyanoacetamide, is described in the literature [9, 10], however the data given in these studies is either contradictory or the structure of the final products was demonstrated insufficiently exhaustively. The product of this interaction **10** is assigned the structure of adduct **A** in [9].



A

In view of the fact that cyanoacetamide may be partially decomposed in the course of the reaction with the liberation of ammonia [6, 7], and proceeding from the data of IR and UV spectroscopy [10] we concluded that the reaction product has not the structure of **A** but is the 4-acetamido derivative of 3-cyanocoumarin **B**, the formation of which is illustrated in the following way.



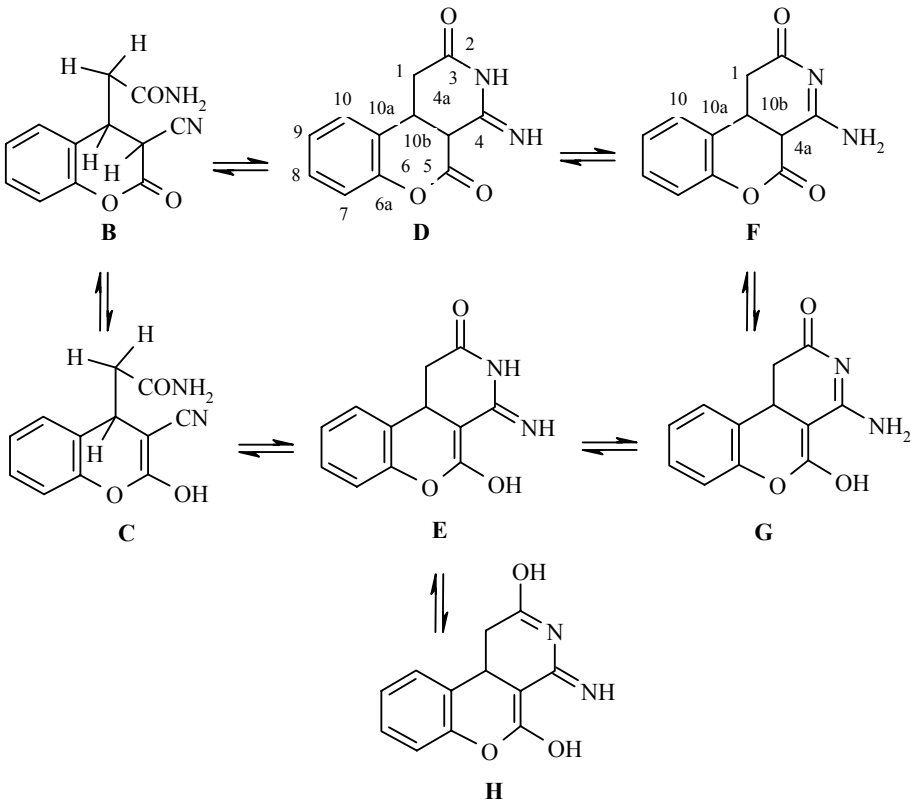
A
$C_{12}H_{10}N_2O_3$
(230)

A¹

B
$C_{12}H_{10}N_2O_3$
(230)

However this does not consider the fact that product **B** may exist in various tautomeric forms due to intramolecular cyclization with participation of the nitrile and amide groups, leading to the formation of derivatives of benzopyrano[3,4-*c*]pyridine.

When establishing the structure of the interaction product of unsubstituted coumarin with cyanoacetamide **10** it is necessary at least to consider the eight possible structures **A**-**H**.



In structures **D-H** some of the protons at saturated bonds are not shown in order to simplify the scheme

With the aim of establishing the true structure of the final product **10**, the reaction of cyanoacetamide with coumarin was carried out under Michael reaction conditions [8], and the structure of its product was studied drawing on a wide selection of spectral methods. The most complete data on its structure were obtained by ^{1}H NMR.

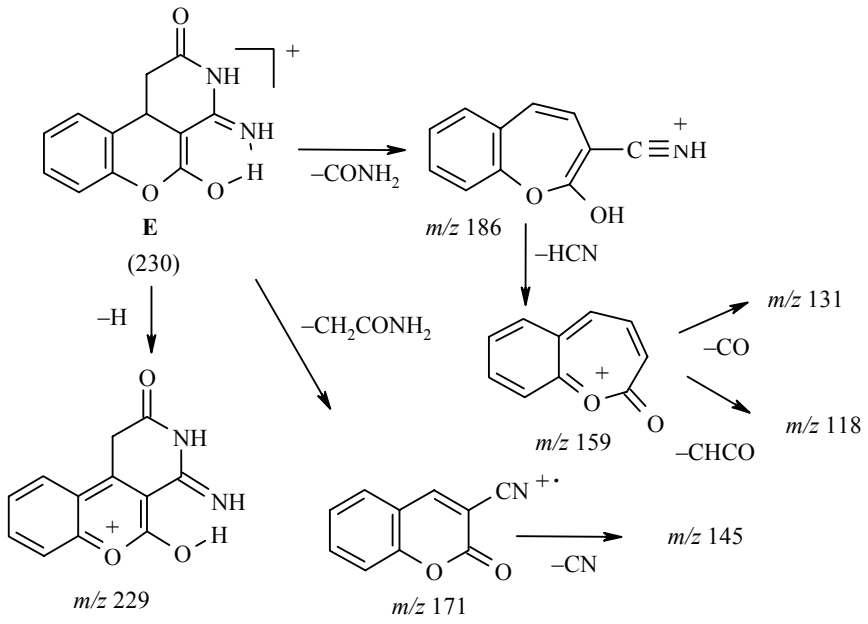
In the ^{1}H NMR spectrum of compound **10** (DMSO-d_6) three quartets were observed in the high field region at 2.44, 3.09, and 4.00 ppm (each of 1 proton intensity). The first two quartets correspond to two nonequivalent methylene protons of a CH_AH_B fragment bonded to the asymmetric C_{10b} atom of the coumarin ring. The geminal coupling constant of these protons is $^2J_{HA,HB}$ = 15.7 Hz.

Each of the methylene protons CH_A (2.44 ppm) and CH_B (3.09 ppm) interacts with the $C_{10b}H$ methine proton (4.00 ppm) with a vicinal coupling constant $^3J_{CHB,C4H}$ = 13.6 and $^3J_{CHB,C4H}$ = 4.6 Hz. The following signals in the ^{1}H NMR spectrum belong to the protons of the coumarin ring, δ, ppm: 7.00 (1H, d, $^3J_{HH}$ = 7.8 Hz, $C_{(7)}H$); 7.15 (1H, t, $^3J_{HH}$ = 7.6 Hz, $C_{(9)}H$); 7.27 (1H, t, $^3J_{HH}$ = 7.7 Hz, $C_{(8)}H$); 7.40 (1H, d, $^3J_{HH}$ = 7.6 Hz, $C_{(10)}H$).

In the low field region of the spectrum a strongly broadened signal was observed at 8.00 (2H intensity) and a singlet at 10.2 ppm (1H intensity), which may belong to protons of the OH or NH type. The absence from the ^{1}H NMR spectrum of a signal for the methine proton at $C_{(3)}$ of the coumarin ring unequivocally excludes structures **B**, **D**, and **F** from consideration. The choice between the remaining bi- and tricyclic structures **C**, **E**, **G**, and **H** is based on consideration of ^{13}C NMR data, in which the following signals are observed (DMSO-d_6), δ, ppm (*J*, Hz): 27.4 (d, $^1J_{C10bH}$ = 130.2, $C_{10b}H$); 38.5 (t, J_{CH_2} = 128.6, CH_2); 72.3 ($C_{(4a)}$); 116.1; 125.0; 127.6; 128.7 ($C_{(10)}H$, $C_{(9)}H$, $C_{(8)}H$, $C_{(7)}H$); 123.7 ($C_{(10a)}$); 148.8 ($C_{(6a)}$); 160.4 (N–CONH); 168.8 (C–CONH).

The obtained data indicate the absence of a signal for the carbon of a CN group, which excludes structures **B** and **C*** from consideration. All the signals observed agree fairly well with the tricyclic tautomeric structures **E**, **G**, and **H**. Structures **E** and **H** seem more preferable since they are stabilized by intramolecular hydrogen bonds. In this case the narrow signal at 10.2 ppm in the ^{1}H NMR spectrum belongs to the OH proton bound in the intramolecular hydrogen bond, and the strongly broadened signal at 8.0 ppm with an intensity of 2 protons belongs either to the two exchanging NH protons of form **E**, or the OH and NH protons of form **H**. Structure **G** is not excluded completely, as these signals may correspond to the OH group (10.2 ppm) and NH group (8.0 ppm).

The absorption band for the CN group was absent from the IR spectrum of compound **10**, which is also in agreement with the data of ^{1}H NMR for the exclusion of structures **A-C** from consideration. From the point of view of data of mass spectrometry of compound **10** on breakdown under conditions of electron impact the structure of tautomeric form **E** is in best agreement. In particular, in the mass spectrum a peak was observed for a molecular ion with mass number 230, which corresponds with the proposed structure. Apart from the molecular peak a series of intense peaks were observed for ions with *m/z* 229 $[M-H]^+$, 186 $[M-CONH_2]^+$, 159 $[M-CONH_2-HCN]^+$, and the peak for the 159 ion had the maximum intensity in the spectrum. Decomposition of structure **E** under conditions of electron impact may be illustrated in the following way.

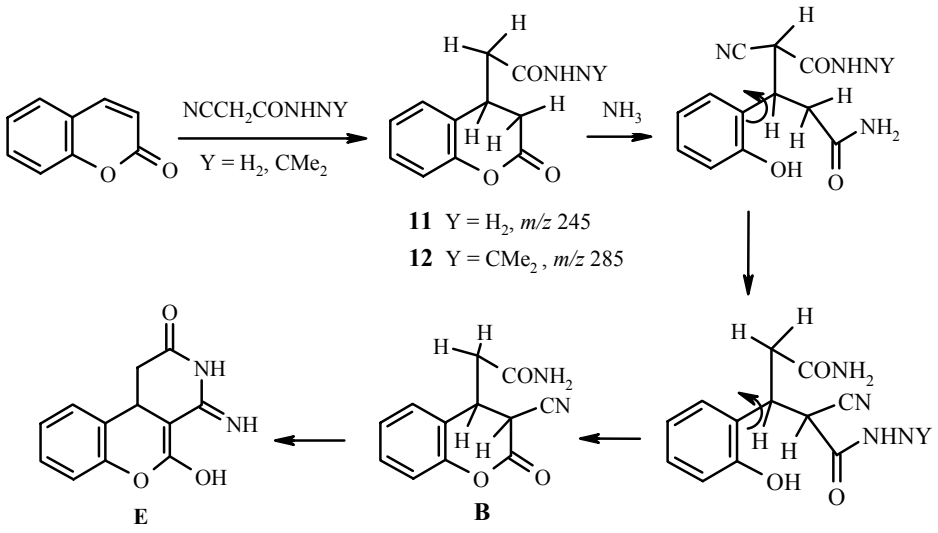


We have therefore shown that the reaction of cyanoacetamide with unsubstituted coumarin leads to product **10**, which, in difference to the data of [9,10], most probably corresponds to a benzopyrano[3,4-*c*]-pyridine derivative in structure, existing preferably in one of the tautomeric forms **E**, **G**, or **H**.

Continuing the study of the interaction of unsubstituted coumarin with analogs of cyanoacetamide, we have carried out the reaction of coumarin with cyanoacetylhydrazine and its isopropylidene derivative. In spite of the fact that actual compounds were not isolated preparatively from the reaction mixtures in these cases, study of the resulting mixtures by mass spectrometry showed that they contain substances with *m/z* 245 (**11**) and 285 (**12**) respectively. These values correspond with the molecular mass of the appropriate Michael adducts.

* The structure of adduct **A** is excluded for the same reason.

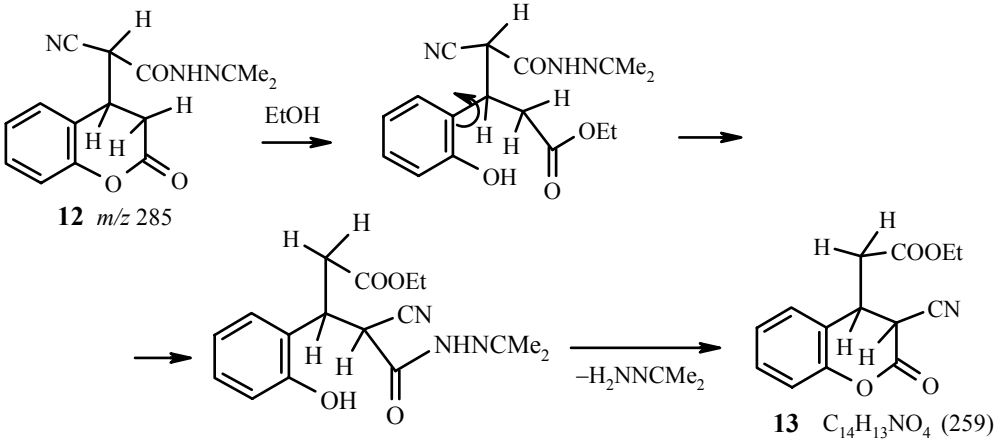
In addition, compounds **11** and **12** are partially transformed under the action of ammonia, which may be formed in the reaction process*, into compounds identical to compound **A**[1], formed from cyanoacetamide and unsubstituted coumarin.



Further recyclization of these compounds with elimination of hydrazine (or its isopropylidene derivative) leads to the formation of compound **B** or one of its tautomeric forms **E**, **G**, **H**. This direction for the reaction is indicated by the presence in the mass spectra of reaction mixtures of a peak for the molecular ion of *m/z* 230 (**B**), and also peaks for all the daughter ions formed in its decomposition.

In the mass spectrum of the reaction mixture obtained from the interaction of the isopropylidene derivative of cyanoacetylhydrazine with coumarin, a peak with *m/z* 245 was recorded corresponding to the product of addition of cyanoacetylhydrazine to coumarin, i.e. compound **11**. This compound may be formed by hydrolysis of the acetonyl group in the course of the reaction both from the initial hydrazine and from the final product **12**.

In the same spectrum a molecular ion peak with *m/z* 259 was observed, which may be attributed to structure **13**, the product of breaking the lactone ring of coumarin **12**, not by the action of ammonia but as a result of ethanolysis (the reaction medium was ethanol) and subsequent recyclization.



* Cyanoacetylhydrazine is capable of decomposing on heating in the presence of base with the liberation of ammonia and like cyanoacetamide may serve as a donor [12].

It has therefore been shown that malonic acid dihydrazide, its N'-isopropylidene and N'-acetyl derivatives, and also ethoxycarbonylacethydrazide react with 3-acyl(3-ethoxycarbonyl or 3-cyano)coumarins in a similar manner to cyanoacetylhydrazine. It was discovered that these reactions proceed under milder conditions than the reaction with analogous derivatives of acetamide. It has been established that the product of the interaction of coumarin with cyanoacetamide exists in the form of a derivative of benzopyrano[3,4-*c*]-pyridine.

EXPERIMENTAL

The mass spectra were recorded on a Finnigan SSQ 710 chromato-mass spectrometer with direct insertion of samples into the ion source. The energy of the ionizing electrons was 70 eV, and ion source temperature was 150°C. The IR spectra were recorded on a Perkin-Elmer 457 instrument in nujol. The ^{1}H NMR spectrum of compound **10** was recorded on a Varian Unity 400 spectrometer (400 MHz), internal standard was TMS.

Reaction mixtures, the compositions of which were studied by mass spectrometry, were obtained by the interaction of malonic acid hydrazide derivatives with 3-substituted coumarins under the conditions indicated previously in [3] after evaporation of the ethanol used as solvent.

Isopropylidene Derivative of 6-Methoxycoumarin-3-carboxylic Acid Hydrazide (5a). Piperidine (1 drop) was added to a suspension of 3-cyano-6-methoxycoumarin (0.17 g, 7.5 mmol) and malonic acid dihydrazide (0.1 g, 7.5 mmol) in ethanol (10 ml) and the mixture boiled with stirring for 10 min. After cooling to room temperature the precipitated solid was filtered off, washed on the filter with cold ethanol (2 × 5 ml), and a light yellow substance (0.1 g) was obtained with mp >300°C (shrivels and darkens at 150°C). The substance obtained was boiled in acetone (15 ml) for 1 h, the solvent was evaporated, and the residue recrystallized from ethanol. A finely crystalline substance (0.05 g, 42%), light yellow with a greenish tinge, was obtained; mp 230-232°C. IR spectrum, ν, cm^{-1}: 1690 (C=O), 1650 (C=N). Found, %: C 60.93; H 4.81; N 10.35. M^+ 274. $C_{14}H_{14}N_2O_4$. Calculated, %: C 61.31; H 5.11; N 10.22. M 274.

Isopropylidene Derivative of 7-Methoxycoumarin-3-carboxylic Acid Hydrazide (5b). Under conditions analogous to those described above a light yellow substance (0.25 g) of mp >300° C was obtained from 7-methoxycoumarin-3-carboxylic acid (0.2 g, 8 mmol) and malonic acid dihydrazide (0.1 g, 7.5 mmol) on boiling the reaction mixture for 1 h. The substance was boiled in acetone (20 ml) for 1 h, the solvent evaporated, and the residue recrystallized from ethanol. A light yellow finely crystalline substance (0.15 g, 51%) of mp 239-241°C was obtained. IR spectrum, ν, cm^{-1}: 1685 (C=O), 1660 (C=N). Found, %: C 61.12; H 4.85; N 9.95. M^+ 274. $C_{14}H_{14}N_2O_4$. Calculated, %: C C 61.31; H 5.11; N 10.22. M 274.

Isopropylidene Derivative of Coumarin-3-carboxylic Acid Hydrazide (5c). Piperidine (1 drop) was added to a mixture of 3-ethoxycarbonylcoumarin (2 g, 9.2 mmol) and N, N'-diisopropylidene malonic acid dihydrazide (0.19 g, 9.2 mmol) in ethanol (15 ml) and the reaction mixture was stirred for 1 h at room temperature. The resulting solid was filtered off, recrystallized from ethanol, and a white crystalline substance (0.14 g, 62.5%) was obtained; mp 200-201°C. IR spectrum, ν, cm^{-1}: 2725 (NH), 1708 (CO), 1608 (C=N). Found, %: C 63.72; H 4.68; N 11.27. M^+ 244. $C_{13}H_{12}N_2O_3$. Calculated, %: C 63.93; H 4.92; N 11.47. M 244.

The yield of compound **5** obtained under analogous conditions from 3-acetylcoumarin was 77%, from 3-cyanocoumarin 53%, and from 3-benzoylcoumarin 77%. All the samples obtained gave no depression of melting point when mixed with a sample obtained previously.

N'-Acetyl Derivative of Coumarin-3-carboxylic Acid Hydrazide (6). Piperidine (1 drop) was added to a mixture of 3-ethoxycarbonylcoumarin (0.2 g, 9.2 mmol) and the N,N'-diacetyl derivative of malonic acid dihydrazide (0.19 g, 9.2 mmol) in ethanol (15 ml) and the reaction mixture was stirred at room temperature for 2 h. The resulting solid was filtered off, recrystallized from ethanol, and a white finely crystalline substance was

obtained (0.2 g, 84%); mp 240-242°C. IR spectrum, ν, cm^{-1}: 2724 (NH), 1718, 1678 (C=O), 1631, 1609 (C=N). Found, %: C 58.27; H 3.98; N 11.10. $M^{+\cdot}$ 246. $C_{12}H_{10}N_2O_4$. Calculated, %: C 58.53; H 4.06; N 11.38. M 246.

The yield of compound **6** obtained under analogous conditions from 3-cyanocoumarin was 78%, and from 3-benzoylcoumarin 80%,. All the samples obtained gave no depression of melting point when mixed with a sample obtained previously.

Coumarin-3-carboxylic Acid Amide (7). Piperidine (1 drop) was added to a mixture of 3-ethoxycarbonylcoumarin (0.2 g, 9.2 mmol) and malonic acid diamide (0.1 g, 9.8 mmol) in ethanol (15 ml), and the mixture was boiled with stirring for 6 h. After cooling to room temperature the resulting precipitate was filtered off, and a finely crystalline white substance (0.15 g, 88%) was obtained; mp 279-281°C (DMF) (lit. mp 280-282°C [13]). Found: $M^{+\cdot}$ 189. Calculated for $C_{10}H_7NO_3$. M 189.

The yield of compound **7** obtained under analogous conditions from 3-acetylcoumarin was 50%, from 3-cyanocoumarin 45%, and from 3-benzoylcoumarin 86%. All the samples obtained gave no depression of melting point when mixed with a sample obtained previously.

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