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SYNTHESIS OF DERIVATIVES OF THE HYDRAZONES OF 5-PHENYLFURO[3,2-*g*]CHROMEN-7-ONES

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Sulfur- and nitrogen-containing derivatives of 5-phenylfurocoumarins at the exocyclic oxygen atom were synthesized. The reaction of the obtained hydrazones with certain carbonyl compounds was investigated.

Keywords: benzopyran-2-thiones, hydrazones, coumarins, semicarbazones, thiosemicarbazones, furocoumarins.

Furocoumarins represent a structurally varied group of natural compounds that are in most cases derivatives of the linear furocoumarin psoralene [1]. The increased interest in the study of furocoumarins is explained by the important role that these compounds play in the vital activity of plant and animal organisms and also by their high and diverse biological activity [2]. Modification of furocoumarin systems is mainly achieved by the introduction of substituents into the furan or benzopyran-2-one fragments of the molecule, while derivatives of furocoumarins at the exocyclic oxygen atom have to this day hardly been studied at all [3].

The aim of the present work was to modify 5-phenylfurocoumarins at the exocyclic oxygen atom with the formation of the corresponding thiones and hydrazones and also to study the reaction of the obtained hydrazones with certain carbonyl compounds.

The 5-phenylfuro[3,2-*g*]chromen-7-ones **1-4** required for the subsequent transformations were obtained by McLeod's reaction from the corresponding 7-hydroxy-4-phenylcoumarins [4]. It is known that direct modification of coumarins at the exocyclic oxygen atom from derivatives of benzopyran-2-one is difficult to achieve. Convenient synthons for the realization of such chemical transformations are derivatives of benzopyran-2-thiones [5, 6].

We used Lawesson's reagent to replace the oxygen atom of the furocoumarin system by a sulfur atom [7, 8]. When 5-phenylfurocoumarins **1-4** were heated with a 10% excess of Lawesson's reagent (LR) in toluene the benzopyran-2-thiones **5-8** were obtained smoothly and with high yields. In contrast to the colorless initial coumarins **1-4** compounds **5-8** were bright-yellow substances, the color of which is due to the presence of C=S group in their molecules.

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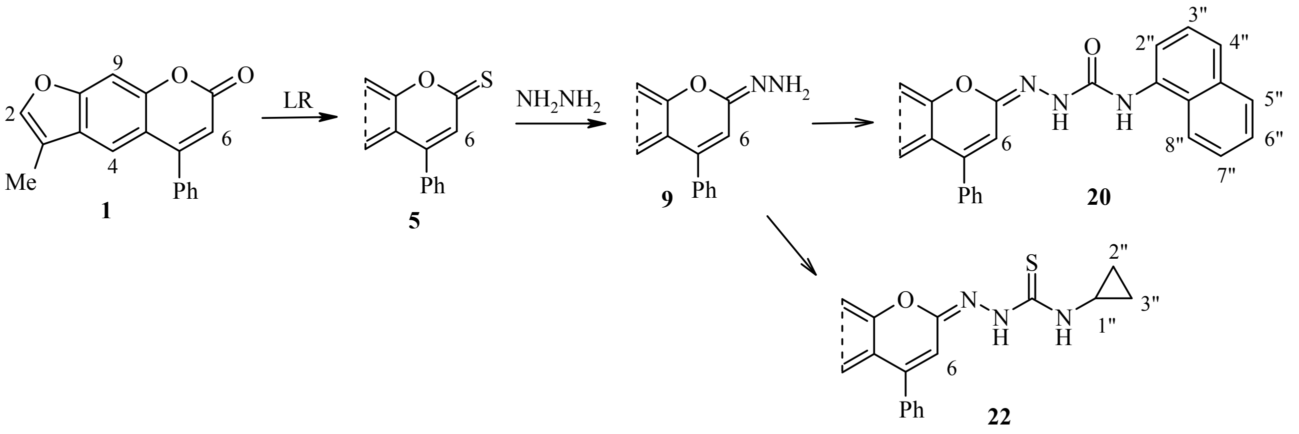
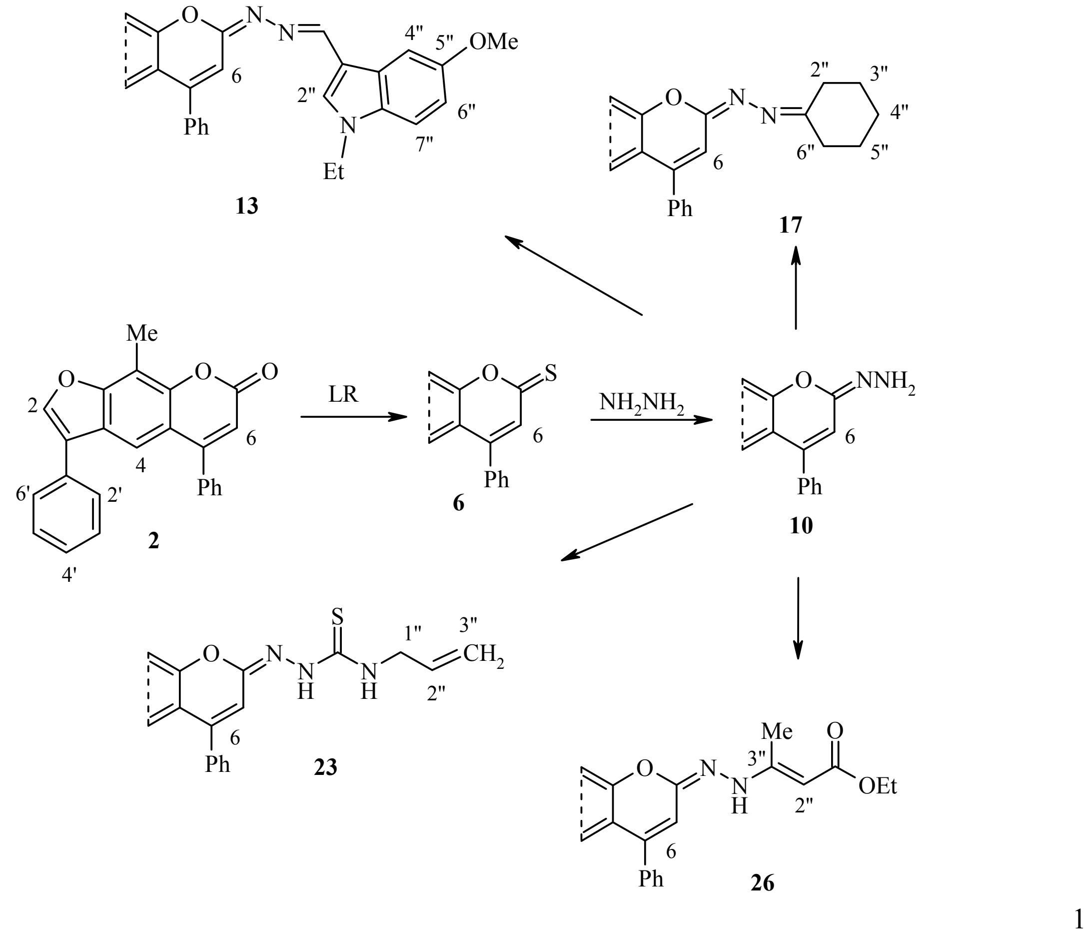
Scheme 1



The furocoumarin hydrazones **9-12** were obtained by treating alcohol solutions of the respective thiones **5-8** with hydrazine hydrate [8,9] (Schemes 1-4).

The structure of the obtained compounds **5-12** is supported by the data from elemental analysis and NMR spectroscopy. In the ^{1}H NMR spectra of the furocoumarins **1-4** the one-proton singlet of the H-6 proton is observed at 6.31-6.44 ppm. The transformation of furocoumarins into furocoumarinthiones **5-8** leads to a downfield shift of the signal for the H-6 proton in the ^{1}H NMR spectra (7.08-7.12 ppm). In the spectra of the hydrazones **9-12** the signal of the H-6 proton is in the region of 6.03-6.16 ppm. Also in the spectra of the hydrazones **9-12** a two-proton broad singlet for the amino group is observed at 5.65-6.05 ppm.

Scheme 2

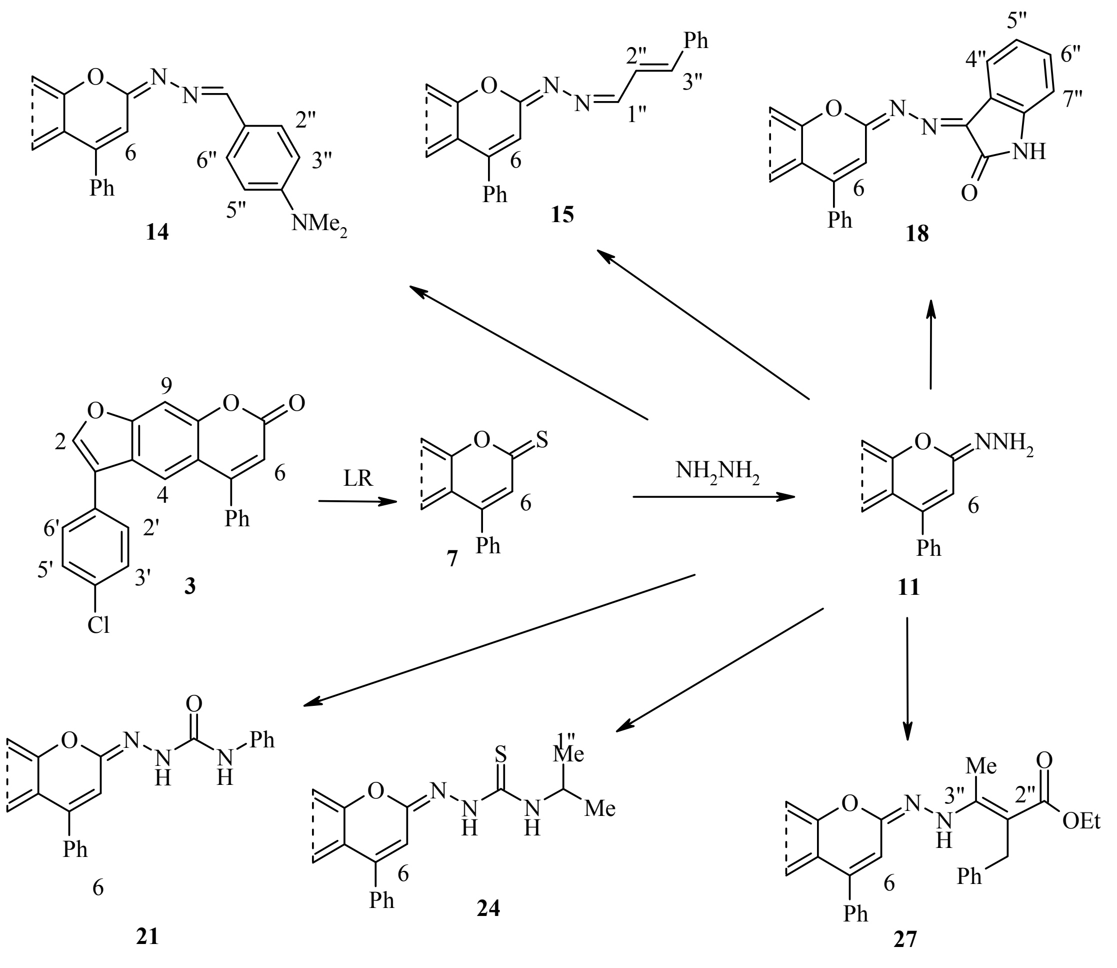


The heating of alcohol solutions of the hydrazones **10-12** with aldehydes (1-ethyl-5-methoxyindole-3-carbaldehyde, 4-(dimethylamino)benzaldehyde, 3-phenylprop-2-enal, and 1-methylindole-3-carbaldehyde) and ketones (cyclohexanone, isatin, acetone) leads to the rapid formation of the corresponding substituted 5-phenylfuro[3,2-*g*]chromen-7-ylidenehydrazones **13-19** (Schemes 2-4). The structure of the obtained derivatives is supported by the data from elemental analysis and NMR spectroscopy. In the ^{1}H NMR of these compounds doubling of the signals for the protons both of the furocoumarin system and of the carbonyl fragment is observed as a result of the existence of the compounds in the form of a mixture of the (*Z*)- and (*E*)-isomers in almost equal amounts.

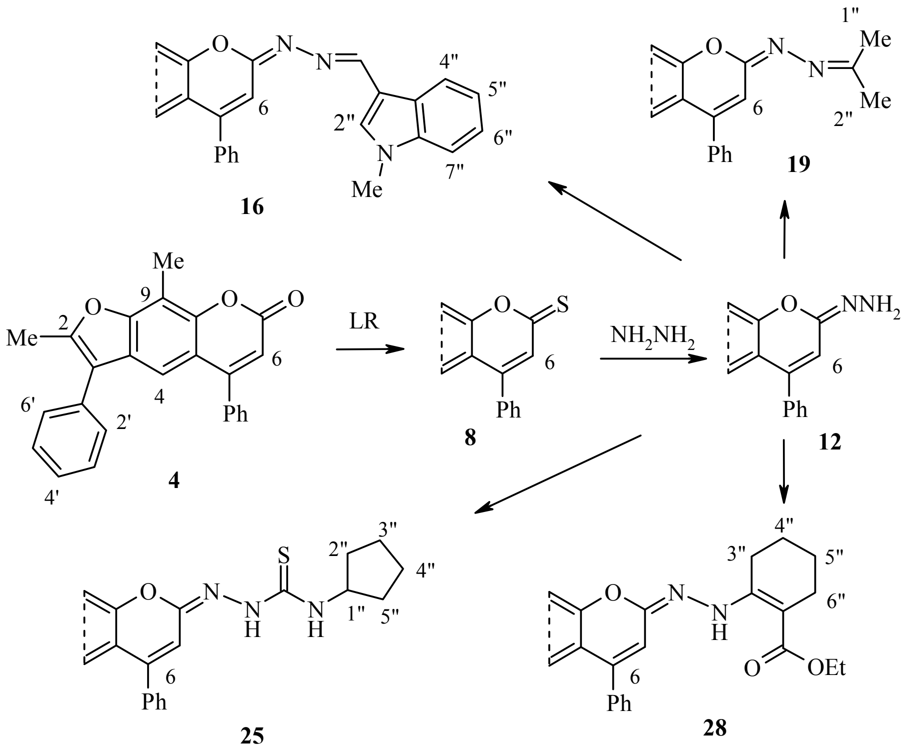
As a result of the reaction of the hydrazones **9-12** with isocyanates (phenyl isocyanate and 1-naphthyl isocyanate) and isothiocyanates (isopropyl, allyl, cyclopropyl, and cyclopentyl isothiocyanates) with heat in dry toluene [10, 11] the corresponding semicarbazones **20** and **21** and thiosemicarbazones **22-25** are formed (Schemes 1-4). In the ^{1}H NMR spectra of compounds **20-25** in the region of 7.20-10.20 ppm there signals for the protons of the NH groups characteristic of semicarbazones and thiosemicarbazones groups.

The reaction of the hydrazones **10-12** with the esters of β-keto acids (acetoacetic ester, ethyl 2-benzyl-acetoacetate and 2-oxocyclohexanecarboxylate) leads to the formation of the enamines **26-28** (schemes 2-4). In the ^{1}H NMR spectra of compounds **26-28** in the region of 11.90-12.74 ppm there is a signal for the proton of the NH group, and for compound **26** there is a singlet for the H-2" proton at 4.67 ppm.

Scheme 3



Scheme 4



EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Varian VXR-300 (300 MHz) and Varian Mercury-400 (400 MHz) instruments in DMSO-d$_6$ for compounds **5-13**, **15-21**, **23**, and **26** and in CDCl$_3$ for compounds **14**, **22**, **24**, **25**, **27**, and **28** with TMS as internal standard. The melting points were determined on a Kofler bench. The course of the reactions and the individuality of the compounds were monitored by TLC on Merck 60 F254 plates with 9:1 and 95:5 chloroform–methanol as eluents.

The synthesis of the initial furocoumarins **1-4** was described in [4].

5-Phenylfuro[3,2-*g*]chromene-7-thiones 5-8 (General Method). A mixture of the furocoumarin **1-4** (10 mmol) and (1.23 g, 5.5 mmol) of Lawesson's reagent in absolute toluene (20 ml) was boiled for 2 h. (The course of the reaction was monitored by TLC.) At the end of the reaction the solvent was evaporated, and the oily residue was crystallized from aqueous 2-propanol.

3-Methyl-5-phenylfuro[3,2-*g*]chromene-7-thione (5). The yield 87%; mp 199-201°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.16 (3H, s, 3-CH$_3$); 7.08 (1H, s, H-6); 7.59 (5H, s, C$_6$H$_5$); 7.64 (1H, s, H-9); 7.81 (2H, s, H-2,4). Found, %: C 74.08; H 4.19; S 10.84. C$_{18}$H$_{12}$O$_2$S. Calculated, %: C 73.95; H 4.14; S 10.97.

9-Methyl-3,5-diphenylfuro[3,2-*g*]chromene-7-thione (6). The yield 95%; mp 267-269°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.76 (3H, s, 9-CH$_3$); 7.12 (1H, s, H-6); 7.34 (1H, m, H-4'); 7.42 (2H, t, *J* = 7.6, H-3',5'); 7.52–7.64 (7H, m, 5-C$_6$H$_5$, H-2',6'); 7.81 (1H, s, H-4); 8.36 (1H, s, H-2). Found, %: C 78.19; H 4.45; S 8.79. C$_{24}$H$_{16}$O$_2$S. Calculated, %: C 78.24; H 4.38; S 8.70.

3-(4-Chlorophenyl)-5-phenylfuro[3,2-*g*]chromene-7-thione (7). The yield 91%; mp 232-234°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.12 (1H, s, H-6); 7.44 (2H, d, *J* = 8.4, H-3',5'); 7.56-7.66 (7H, m, 5-C$_6$H$_5$, H-2',6'); 7.94 (1H, s, H-9); 7.97 (1H, s, H-4); 8.42 (1H, s, H-2). Found, %: C 71.01; H 3.49; Cl 9.28; S 8.32. C$_{23}$H$_{13}$ClO$_2$S. Calculated, %: C 71.04; H 3.37; Cl 9.12; S 8.25.

2,9-Dimethyl-3,5-diphenylfuro[3,2-*g*]chromene-7-thione (8). The yield 95%; mp 289-291°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.59 (3H, s, 2-CH_3); 2.73 (3H, s, 9-CH_3); 7.08 (1H, s, H-6); 7.34 (1H, m, H-4'); 7.39-7.57 (10H, m, H-4, 5-C_6H_5, H-2',3',5',6'). Found, %: C 78.63; H 4.81; S 8.32. $C_{25}H_{18}O_2S$. Calculated, %: C 78.51; H 4.74; S 8.38.

5-Phenylfuro[3,2-*g*]chromen-7-ones Hydrazones 9-12 (General Method). To a solution of the furocoumarinthione **5-8** (10 mmol) in ethanol (30 ml) we added hydrazine hydrate (1 ml, 20 mmol). The mixture was boiled for 2 h. (The course of the reaction was monitored by TLC). When the reaction had finished the mixture was cooled to room temperature, and the precipitate was filtered off and recrystallized from 2-propanol.

3-Methyl-5-phenylfuro[3,2-*g*]chromen-7-one Hydrazone (9). The yield 73%; mp 148-149°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.09 (3H, s, 3-CH_3); 5.70 (2H, br. s, NH_2); 6.03 (1H, s, H-6); 7.16 (1H, s, H-9); 7.30 (1H, s, H-4); 7.41-7.52 (5H, m, C_6H_5); 7.55 (1H, d, *J* = 1.2, H-2). Found, %: C 74.58; H 4.94; N 9.66. $C_{18}H_{14}N_2O_2$. Calculated, %: C 74.47; H 4.86; N 9.65.

9-Methyl-3,5-diphenylfuro[3,2-*g*]chromen-7-one Hydrazone (10). The yield 87%; mp 203-204°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.76 (3H, s, 9-CH_3); 5.70 (2H, br. s, NH_2); 6.08 (1H, s, H-6); 7.28 (1H, m, H-4'); 7.34-7.50 (10H, m, H-4, 5-C_6H_5, H-2',3',5',6'); 8.10 (1H, s, H-2). Found, %: C 78.81; H 4.98; N 7.58. $C_{24}H_{18}N_2O_2$. Calculated, %: C 78.67; H 4.95; N 7.65.

3-(4-Chlorophenyl)furo-5-phenyl[3,2-*g*]chromen-7-one Hydrazone (11). The yield 76%; mp 193-194°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.05 (2H, br. s, NH_2); 6.16 (1H, s, H-6); 7.45-7.55 (11H, m, H-4, 5-C_6H_5, H-9, H-2',3',5',6'); 8.35 (1H, s, H-2). Found, %: C 71.59; H 4.06; Cl 9.11; N 7.35. $C_{23}H_{15}ClN_2O_2$. Calculated, %: C 71.41; H 3.91; Cl 9.16; N 7.24.

2,9-Dimethyl-3,5-diphenylfuro[3,2-*g*]chromen-7-one Hydrazone (12). The yield 72%; mp 234-235°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.49 (3H, s, 2-CH_3); 2.53 (3H, s, 9-CH_3); 5.65 (2H, br. s, NH_2); 6.03 (1H, s, H-6); 7.08 (1H, s, H-4); 7.25-7.45 (10H, m, 3-C_6H_5, 5-C_6H_5). Found, %: C 79.05; H 5.38; N 7.29. $C_{25}H_{20}N_2O_2$. Calculated, %: C 78.93; H 5.30; N 7.36.

(5-Phenylfuro[3,2-*g*]chromen-7-ylidene)hydrazones of Aldehydes 13-16 and Ketones 17-19 (General Method). A mixture of the hydrazone **10-12** (2 mmol) and respective aldehyde or ketone (2.2 mmol) in ethanol (10 ml) was boiled for 2-4 h. (The course of the reaction was monitored by TLC.) When the reaction had finished the mixture was cooled to room temperature, and the precipitate was filtered off and recrystallized from 2-propanol.

1-Ethyl-5-methoxyindole-3-carbaldehyde (9-Methyl-3,5-diphenylfuro[3,2-*g*]chromen-7-ylidene)-hydrazone (13). The yield 78%; mp 268-269°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.38-1.49 (3H, m, $CH_2C\underline{H}_3$); 2.60 and 2.76 (3H, two s, 9-CH_3); 3.70 and 3.72 (3H, two s, 5''-CH_3O); 4.16-4.29 (2H, m, $C\underline{H}_2CH_3$); 6.41 and 7.35 (1H, s, H-6); 6.43 and 6.86 (1H, two d, *J* = 2.4, H-4''); 7.36-7.62 (12H, m, 3-C_6H_5, 5-C_6H_5, H-6'',7''); 7.74 and 7.88 (1H, two s, H-4); 7.82 and 8.08 (1H, two s, H-2''); 8.27 and 8.29 (1H, two s, H-2); 8.60 and 8.64 (1H, two s, N=CH). Found, %: C 78.69; H 5.29; N 7.69. $C_{36}H_{29}N_3O_3$. Calculated, %: C 78.38; H 5.30; N 7.62.

4-(Dimethylamino)benzaldehyde [3-(4-Chlorophenyl)-5-phenylfuro[3,2-*g*]chromen-7-ylidene]-hydrazone (14). The yield 72%; mp 272-273°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.06 (6H, s, $N(CH_3)_2$); 6.46 (1H, s, H-6); 6.75 (2H, d, *J* = 8.8, H-3'',5''); 7.38 (2H, d, *J* = 8.8, H-3',5'); 7.42 (2H, d, *J* = 8.8, H-2',6'); 7.50 (5H, m, 5-C_6H_5); 7.60 (1H, s, H-9); 7.67 (1H, s, N=CH); 7.76 (1H, s, H-4); 7.78 (2H, d, *J* = 8.8, H-2'',6''); 8.39 (1H, s, H-2). Found, %: C 74.16; H 4.69; Cl 6.89; N 8.19. $C_{32}H_{24}ClN_3O_2$. Calculated, %: C 74.20; H 4.67; Cl 6.84; N 8.11.

3-Phenylprop-2-enal [3-(4-chlorophenyl)-5-phenylfuro[3,2-*g*]chromen-7-ylidene]hydrazone (15). The yield 83%; mp 265-266°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.46 and 7.21 (1H, two s, H-6); 7.15-7.67 (17H, m, H-9, 5-C_6H_5, H-2',3',5',6', H-1'',2'', C_6H_5); 7.73 and 7.78 (1H, two s, H-4); 8.22 and 8.25 (1H, two d, *J* = 8.8, H-3''); 8.40 and 8.42 (1H, two s, H-2). Found, %: C 76.64; H 4.18; Cl 7.01; N 5.61. $C_{32}H_{21}ClN_2O_2$. Calculated, %: C 76.72; H 4.23; Cl 7.08; N 5.59.

1-Methylindole-3-carbaldehyde [2,9-Dimethyl-3,5-diphenylfuro[3,2-*g*]chromen-7-ylidene]hydrazone (16). The yield 85%; mp 278-279°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.60 and 2.71 (6H, two s, 2,9-CH_3); 3.83 and 3.87 (3H, two s, NCH_3); 6.35 and 7.22 (1H, s, H-6); 7.12-7.56 (14H, m, 3-C_6H_5, H-4, 5-C_6H_5, H-5",6",7"); 7.83 and 7.84 (1H, two s, H-2"); 8.14 and 8.62 (1H, two d, *J* = 7.2, H-4"); 8.61 and 8.65 (1H, two s, N=CH). Found, %: C 80.67; H 5.29; N 7.97. $C_{35}H_{27}N_3O_2$. Calculated, %: C 80.59; H 5.22; N 8.06.

9-Methyl-3,5-diphenylfuro[3,2-*g*]chromen-7-one Cyclohexylidenehydrazone (17). The yield 59%; mp 196-197°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.48-1.75 (6H, m, 3",4",5"-CH_2); 2.37-2.76 (4H, m, 2",6"-CH_2); 2.61 and 2.66 (3H, two s, 9-CH_3); 6.35 and 7.03 (1H, two s, H-6); 7.33-7.56 (11H, m, 3-C_6H_5, H-4, 5-C_6H_5); 8.35 and 8.36 (1H, s, H-2). Found, %: C 80.75; H 5.96; N 6.32. $C_{30}H_{26}N_2O_2$. Calculated, %: C 80.69; H 5.87; N 6.27.

3-[3-(4-Chlorophenyl)-5-phenylfuro[3,2-*g*]chromen-7-ylidene]hydrazono-1,3-dihydroindol-2-one (18). The yield 89%; mp 269-270°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.84 and 7.29 (1H, two s, H-6); 6.85 and 6.87 (1H, two d, *J* = 7.2, H-7"); 6.91 and 7.00 (1H, two t, *J* = 7.2, H-5"); 7.30-7.77 (11H, m, 5-C_6H_5, H-9, H-2',3',5',6', H-6"); 7.86 and 7.94 (1H, two s, H-4); 8.24 and 8.28 (1H, two d, *J* = 7.6, H-4"); 8.40 and 8.42 (1H, two s, H-2); 10.55 and 10.63 (1H, two s, NH). Found, %: C 72.21; H 3.57; Cl 6.90; N 8.18. $C_{31}H_{18}ClN_3O_3$. Calculated, %: C 72.17; H 3.52; Cl 6.87; N 8.14.

2,9-Dimethyl-3,5-diphenylfuro[3,2-*g*]chromen-7-one (1-Methylethylidene)hydrazone (19). The yield 56%; mp 219-220°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.92 (3H, s, 1"-CH_3); 2.02 and 2.03 (3H, two s, 2-CH_3); 2.09 (3H, s, 2"-CH_3); 2.61 and 2.65 (3H, two s, 9-CH_3); 6.30 and 6.96 (1H, two s, H-6); 7.17 and 7.19 (1H, two s, H-4); 7.34-7.54 (10H, m, 3-C_6H_5, 5-C_6H_5). Found, %: C 80.09; H 5.71; N 6.49. $C_{28}H_{24}N_2O_2$. Calculated, %: C 79.98; H 5.75; N 6.66.

(5-Phenylfuro[3,2-*g*]chromen-7-ylidene)hydrazones Semicarbazones and Thiosemicarbazones 20-25 (General Method). A mixture of hydrazone **9-12** (2 mmol) and the respective isocyanate or isothiocyanate (2.2 mmol) in dry toluene (10 ml) was boiled for 2 h. (The course of the reaction was monitored by TLC). When the reaction had finished the mixture was cooled to room temperature, and the precipitate was filtered off and recrystallized from 2-propanol.

3-Methyl-5-phenylfuro[3,2-*g*]chromen-7-one N-(1-Naphthyl)semicarbazone (20). The yield 56%; mp 236-237°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.11 (3H, s, 3-CH_3); 6.46 (1H, s, H-6); 7.35 (1H, s, H-9); 7.48-7.69 (11H, m, H-4, 5-C_6H_5, H-3",4",5",6",7"); 7.82 (1H, s, H-2); 7.96 (1H, d, *J* = 8.4, H-2"); 8.06 (1H, d, *J* = 8.4, H-8"); 9.09 and 10.23 (2H, two s, HNCONH). Found, %: C 75.91; H 4.65; N 9.02. $C_{29}H_{21}N_3O_3$. Calculated, %: C 75.80; H 4.61; N 9.14.

3-(4-Chlorophenyl)-5-phenylfuro[3,2-*g*]chromen-7-one N-Phenylsemicarbazone (21). The yield 92%; mp 269-270. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.32 (1H, s, H-6); 7.06-7.55 (15H, m, H-9, 5-C_6H_5, H-2',3',5',6', C_6H_5); 7.64 (1H, s, H-4); 7.78 (1H, s, H-2); 8.09 and 8.37 (2H, two s, HNCONH). Found, %: C 71.28; H 3.91; Cl 7.12; N 8.30. $C_{30}H_{20}ClN_3O_3$. Calculated, %: C 71.22; H 3.98; Cl 7.01; N 8.31.

3-Methyl-5-phenylfuro[3,2-*g*]chromen-7-one N-Cyclopropylthiosemicarbazone (22). The yield 58%; mp 222-223°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.70-0.92 (4H, m, 2",3"-CH_2); 2.13 (3H, s, 3-CH_3); 3.18 (1H, m, H-1"); 6.19 (1H, s, H-6); 7.32-7.55 (9H, m, H-2,4, 5-C_6H_5, H-9, CSNH); 9.14 (1H, s, NNHCS). Found, %: C 67.56; H 5.48; N 10.70; S 8.26. $C_{22}H_{19}N_3O_2S$. Calculated, %: C 67.85; H 4.92; N 10.79; S 8.23.

9-Methyl-3,5-diphenylfuro[3,2-*g*]chromen-7-one N-Allylthiosemicarbazone (23). The yield 86%; mp 232-233°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.64 (3H, s, 9-CH_3); 4.22 (2H, t, *J* = 5.6, 1"-CH_2); 5.11 (1H, dd, *J* = 1.6, *J* = 10.4, H-3"*cis*); 5.17 (1H, dd, *J* = 1.6, *J* = 17.6, H-3"*trans*); 5.89-5.97 (1H, m, H-2"); 6.28 (1H, s, H-6); 7.34-7.55 (11H, m, 3-C_6H_5, H-4, 5-C_6H_5); 8.38 (1H, s, H-2); 8.42 (1H, t, *J* = 5.6, CSNH); 10.03 (1H, s, NNHCS). Found, %: C 72.11; H 5.03; N 8.87; S 6.93. $C_{28}H_{23}N_3O_2S$. Calculated, %: C 72.23; H 4.98; N 9.03; S 6.89.

3-(4-Chlorophenyl)-5-phenylfuro[3,2-*g*]chromen-7-one N-Isopropylthiosemicarbazone (24). The yield 73%; mp 218-219°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.33 (6H, d, *J* = 7.6, $CH(C\underline{H}_3)_2$); 4.56-4.62

(1H, m, $C\underline{H}(CH_3)_2$); 6.27 (1H, s, H-6); 7.18 (1H, d, *J* = 5.6, CSNH); 7.35-7.54 (10H, m, 5-C_6H_5, H-9, H-2',3',5',6'); 7.64 (1H, s, H-4); 7.79 (1H, s, H-2); 9.05 (1H, s, NNHCS). Found, %: C 66.53; H 4.51; Cl 7.32; N 8.55; S 6.63. $C_{27}H_{22}ClN_3O_2S$. Calculated, %: C 66.45; H 4.54; Cl 7.26; N 8.61; S 6.57.

2,9-Dimethyl-3,5-diphenylfuro[3,2-*g*]chromen-7-one N-Cyclopentylthiosemicarbazone (25). The yield 72%; mp 268-269°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.45-1.80 (8H, m, H-2",3",4",5"-CH_2); 2.54 (3H, s, 2-CH_3); 2.64 (3H, s, 9-CH_3); 4.71-4.80 (1H, m, H-1"); 6.21 (1H, s, H-6); 7.26-7.48 (12H, m, 3-C_6H_5, H-4, 5-C_6H_5, CSNH); 8.93 (1H, s, NNHCS). Found, %: C 73.46; H 5.71; N 8.29; S 6.30. $C_{31}H_{29}N_3O_2S$. Calculated, %: C 73.34; H 5.76; N 8.28; S 6.32.

Ethyl 3-[2-(5-Phenylfuro[3,2-*g*]chromen-7-ylidene)hydrazinyl]but-2-enoates 26-28 (General Method). A mixture of hydrazone **10-12** (2 mmol) and respective β-keto ester (2.2 mmol) in ethanol (10 ml) was boiled for 4-6 h. (The course of the reaction was monitored by TLC). When the reaction had finished the mixture was cooled to room temperature and recrystallized from 2-propanol.

Ethyl 3-[2-(9-Methyl-3,5-diphenylfuro[3,2-*g*]chromen-7-ylidene)hydrazinyl]but-2-enoate (26). The yield 72%; mp 181-182°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.23 (3H, t, *J* = 7.2, 2''' -CH_3); 2.13 (3H, s, 3"-CH_3); 2.68 (3H, s, 9-CH_3); 4.12 (2H, q, *J* = 7.2, 1'''-CH_3); 4.67 (1H, s, H-2"); 6.30 (1H, s, H-6); 7.34-7.55 (11H, m, 3-C_6H_5, H-4, 5-C_6H_5); 8.35 (1H, s, H-2); 11.90 (1H, s, NH). Found, %: C 75.38; H 5.56; N 5.79. $C_{30}H_{26}N_2O_4$. Calculated, %: C 75.30; H 5.48; N 5.85.

Ethyl 2-Benzyl-3-{2-[3-(4-chlorophenyl)-5-phenylfuro[3,2-*g*]chromen-7-ylidene]hydrazinyl}but-2-enoate (27). The yield 69%; mp 178-179°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.26 (3H, m, $CH_2C\underline{H}_3$); 2.26 (3H, s, 3"-CH_3); 3.75 (2H, s, 2"-CH_2); 4.22 (2H, m, $C\underline{H}_2CH_3$); 6.29 and 6.40 (1H, two s, H-6); 7.18-7.54 (15H, m, H-9, 5-C_6H_5, H-2',3',5',6', C_6H_5); 7.57 and 7.60 (1H, two s, H-4); 7.74 and 7.77 (1H, two s, H-2); 12.74 (1H, s, NH). Found, %: C 73.46; H 5.03; Cl 6.09; N 4.68. $C_{36}H_{29}ClN_2O_4$. Calculated, %: C 73.40; H 4.96; Cl 6.02; N 4.76.

Ethyl 2-[2-(2,9-Dimethyl-3,5-diphenylfuro[3,2-*g*]chromen-7-ylidene)hydrazinyl]cyclohex-1-ene-1-carboxylate (28). The yield 84%; mp 234-235°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.32 (3H, t, *J* = 7.2, $CH_2C\underline{H}_3$); 1.62-1.74 (4H, m, 4",5"-CH_2); 2.37 (2H, m, 3"-CH_2); 2.54 (3H, s, 2-CH_3); 2.69 (2H, m, 6"-CH_2); 2.76 (3H, s, 9-CH_3); 4.23 (2H, q, *J* = 7.2, $C\underline{H}_2CH_3$); 6.22 (1H, s, H-6); 7.22-7.46 (11H, m, 3-C_6H_5, H-4, 5-C_6H_5); 12.34 (1H, s, NH). Found, %: C 76.58; H 6.13; N 5.21. $C_{34}H_{32}N_2O_4$. Calculated, %: C 76.67; H 6.06; N 5.26.

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