ONE-POT SYNTHESIS OF N-(3-COUMARINOYL-)-N'-(SALICYLIDENE)HYDRAZINES FROM 3-ETHOXYCARBONYL-(ACYL)COUMARINS

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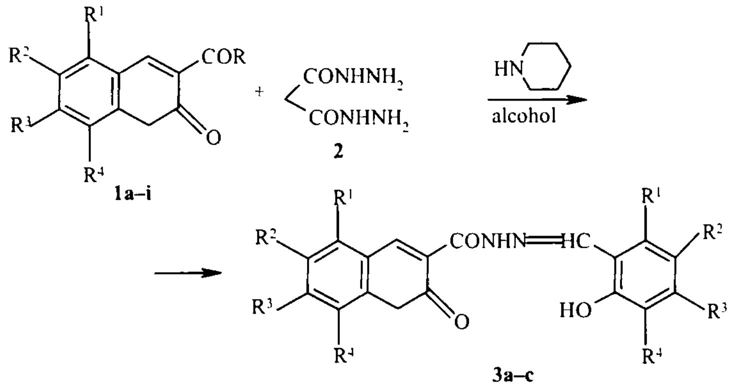
Earlier we established that reaction of 3-ethoxycarbonyl(acyl)coumarins with cyanoacetylhydrazine and its N-derivatives under Michael reaction conditions leads to synthesis of 3-cyanocoumarins [1,2]. In an extension of this research, under similar conditions (ethanol, 70-75°C, catalytic amounts of piperidine), we have studied the reaction of 3-ethoxycarbonyl-, 3-acetyl-, and 3-benzoylcoumarins **1a-c** and also their 6-methyl- and 6(8)-methoxy-substituted derivatives **1d-i** with malonic acid dihydrazide **2**. We have established that N'-salicylidene derivatives of coumarin-3-carboxylic acid hydrazide **3a-c** are formed as a result of this reaction.



1a R = OC_2H_5, R^{1-4} = H; **1b** R = CH^3, R^{1-4} = H; **1c** R = C_6H_5, R^{1-4} = H;
1d R = OC_2H_5, R^3 = CH_3, $R^{1,2,4}$ = H; **1e** R = R^2 = CH_3, $R^{1,3,4}$ = H;
1f R = C_6H_5, R^2 = CH_3, $R^{1,3,4}$ = H; **1g** R = OC_2H_5, R^4 = OCH_3, $R^{1,2,3}$ = H;
1h R = CH_3, R^4 = OCH_3, $R^{1,2,3}$ = H; **1i** R = C_6H_5, R^4 = OCH_3, $R^{1,2,3}$ = H;
3a R^{1-4} = H; **3b** R^2 = CH_3, $R^{1,2,3}$ = H; **3c** R^4 = OCH_3, $R^{1,2,3}$ = H

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The spectral characteristics (IR, ^{1}H NMR, and mass spectra) and also elemental analysis data do not contradict the structure proposed for compounds **3a-c**. Comparison of the properties of compound **3a** with the properties of the compound synthesized by reaction of salicylic aldehyde with cyanoacetylhydrazine followed by acid hydrolysis [3], for which the structure of N-(3-coumarinoyl)-N'-(salicylidene)hydrazine has been proven, showed that they are completely identical (no depression of the melting point for a mixed sample, identical IR and ^{1}H NMR spectra).

Formation of compounds **3a-c** can be considered as the result of reaction of the initially formed coumarin-3-carboxylic acid hydrazide with the starting coumarin at the 4 position, followed by opening of the lactone ring of the 3,4-dihydrocoumarin derivative formed and finally cleavage of a molecule of malonic ester or the corresponding β-keto ester, depending on the structure of the starting coumarin.

Compounds **3a-c** are high-melting, light yellow, finely crystalline materials which are stable when stored. The following list gives the compound, the melting point (°C), the average yield (in %), M^+ (from mass spectra): **3a**, 294-296°C (DMF), 43%; M^+ 308; calculated for $C_{17}H_{12}N_2O_4$: 308. **3b**, 292-294°C (DMF), 65%, M^+ 336; calculated for $C_{19}H_{16}N_2O_4$: 336. **3c**, 270-272°C (DMF), 56%, M^+ 368; calculated for $C_{19}H_{16}N_2O_6$: 368.

The observed conversion of coumarins **1a-i** substituted at the 3 position by electron-acceptor groups to coumarin-3-carboxylic acid hydrazide derivatives is one more example of a rearrangement similar to what occurs in synthesis of 3-cyanocoumarins by the method we described earlier [1,2].

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