# SYNTHESIS OF 3-NITRO-4-AMINO-
# AND 3,4-DIAMINO-1-THIACOUMARINS

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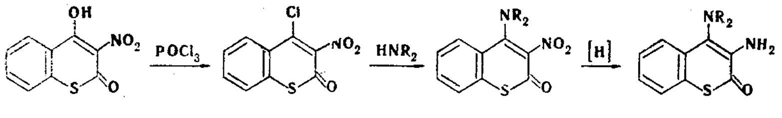
We have synthesized the previously unknown 3-nitro-4-amino- (I) and 3,4-diamino-1-thiacoumarins (II) from 3-nitro-4-hydroxy-1-thiacoumarin (III) through 3-nitro-4-chloro-1-thiacoumarin (IV), which we prepared for the first time.



III IV I II

I, II $NR_2=NH_2$, $n$-$C_4H_9NH$, $(CH_3)_3CNH$ $(C_2H_5)_2N$, $C_6H_5NH$

Chloro derivative IV is formed smoothly in 93% yield in the reaction of III with phosphorus oxychloride in dimethylformamide (DMF). The labile chlorine atom in thiacoumarin IV is readily replaced by ammonia and aliphatic, aromatic, and heterocyclic amine residues to give compounds of the I type in almost quantitative yields. Compounds II were obtained in 70-80% yields by hydrogenation of nitro compound I over $Pd/BaSO_4$ or Raney nickel in alcohol. None of the synthesized I form salts with dilute acids and alkalis, II gives salts with dilute acids. The IR spectrum of a chloroform solution of IV contains bands at 1650 (C = O), 1595 (double bonds of the thiacoumarin ring), and 1540 and 1320 $cm^{-1}$ ($\nu_{as}$ and $\nu_s$ of the $NO_2$ group). In addition to the stretching vibrations of a $NO_2$ group, absorption bands of a C = O group (1610-1630 $cm^{-1}$) and of the double bonds of a thiacoumarin ring (1580-1590 $cm^{-1}$) appear in the IR spectra of I. Absorption bands are observed at 3480 and 3370 $cm^{-1}$ ($\nu_{as}$ and $\nu_s$ of the amino groups) and broad intense bands at 1580-1590 $cm^{-1}$, which are related to the vibrations of a carbonyl group and the double bonds of a thiacoumarin ring, are observed in the IR spectra of diamines II. Thus the frequencies of the carbonyl group in the spectra of the compounds obtained in this research are considerably lower than those of their oxygen analogs [1], and this is in agreement with the literature data on the IR spectra of coumarin and thiacoumarin. The results of elementary analysis of I, II, and IV are in agreement with the calculated values. Compounds I and II may be of interest for a study of the mutual effect of the sulfur atom of the heteroring, the carbonyl group, and sutstituents in the 3 position on the spectral characteristics, ionization constants, and tautomeric relationships, particularly as compared with their oxygen analogs.

## LITERATURE CITED

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