

## SYNTHESIS AND PROPERTIES OF 4-CHLOROMETHYL-6-HYDROXY- COUMARINS AND 4-(2-BENZOFURYL)- 6-HYDROXYCOUMARINS

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*New 4-chloromethyl-6-hydroxycoumarins have been obtained by the condensation of hydroquinone derivatives with 4-chloroacetoacetic ester, and have been used for the synthesis of 4-(2-benzofuryl)-6-hydroxycoumarins. Alkylation and acylation of the phenolic hydroxyl of the synthesized 4-(2-benzofuryl)coumarins have been investigated.*

**Keywords:** 4-(2-benzofuryl)coumarins, 4-chloromethylcoumarins, alkylation, acylation, heterocyclization.

4-Halomethylcoumarins, which may be obtained under the conditions of the Pechmann reaction [1-3] by the chlorination of derivatives of coumarin-4-acetic acid in AcOH [4] and by the interaction of 4-hydroxymethylcoumarins with  $\text{PCl}_5$  in benzene [5], are convenient reactants for the synthesis of various heterocyclic compounds. Substituted chloromethylcoumarins are converted into derivatives of 3-benzofurylacetic acid by the action of alkalis [6]. The alkylation of amines and phenols by substituted 4-halomethylcoumarins is known [7-11].

Various methods have been described for the synthesis of 4-(2-benzofuryl)coumarins including alkylation with 4-halomethylcoumarins of salicylaldehyde derivatives [12-15], of 2-hydroxyacetophenone [16], or methyl salicylate [16] with subsequent intramolecular cyclization of the methylene and carbonyl groups, interaction of 2-(2-hydroxybenzoyl)benzofuran with ethyl (triphenylphosphorylidene)acetate [13], or Pechmann condensation of resorcinol with 2-benzofuroylacetic ester [13]. At the present moment only the last method permits derivatives of 2-benzofurylcoumarin containing a free hydroxyl group to be obtained.

In this connection it was of interest to study the possibility of using 4-(2-benzofuryl)hydroxycoumarins without previous protection of the phenolic hydroxyl group for the synthesis of 4-chloromethylcoumarins. To achieve this aim we synthesized the new 4-chloromethyl-6-hydroxycoumarins **1a-c**, and also used the previously described 4-chloromethyl-7-hydroxycoumarins **1d,e** [6].

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