2-Acetyl-4,4,6-trimethylcyclohexane-1,3-dione - (±)-Angustione (III). When 10 mmole of LDA in 15 ml of THF was used, 4 mmole of 4,6-dimethyl-2-[1'-(N-pyrrolidyl)ethylidene]cyclohexane-1,3-dione (VII) and 10 mmole of methyl iodide gave 0.35 g (45%) of compound (III).

4,4,6-Trimethyl-2-[1'-(N-pyrrolidyl)ethylidene]cyclohexane-1,3-dione (IX). From 1 mmole of 2-acetyl-4,4,6-trimethylcyclohexane-1,3-dione (III) and an equimolar amount of pyrrolidine, by boiling in benzene with a Dean-Stark trap, 0.2 g (80%) of compound (IX) was obtained.

Copper Complex of the Diketone (III). A solution of 1 mmole of 2-acetyl-4,4,6-trimethylcyclohexane-1,3-dione (III) in 5 ml of ether was stirred with 5 ml of saturated copper acetate solution for 30 min. The organic layer was separated off and the aqueous layer was extracted with ether (3 x 10 ml). The combined extracts were dried over Na₂SO₄. The solvent was driven off in vacuum. The residue was crystallized from hexane. This gave 0.11 g of the copper complex, mp 201-202°C; according to the literature, mp 201-202°C [5].

LITERATURE CITED

BROMINATION OF EMODIN

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Using emodin as an example, it has been shown that in the bromination of hydroxyanthraquinones the qualitative composition and quantitative ratio of the reaction products depend on the nature of the brominating agent and the solvent, the ratio of the reagents, and the temperature regime. In order to obtain bromo-3-methyl-1,6,8-trihydroxyanthraquinone it is recommended to use dioxane dibromide in acid solution as the brominating agent, and to obtain 5-bromo-3-methyl-1,6,8-trihydroxyanthraquinone the same reagent in dioxane solution. The optimum conditions for obtaining 3-bromomethyl-1,6,8-trihydroxyanthraquinone by the methods of initiated bromination and photobromination have been selected.

Halogen derivatives of hydroxyanthraquinones are promising intermediates in the synthesis of biologically active compounds [1]. Depending on the conditions, halogenation is possible in the side chains and in the aromatic nucleus (α- or β-position); however, it is impossible to achieve a strictly selective process [2]. Because of the dissimilar reactivities of the rings, in an excess of halogenating agent up to eight α-, β-, and α,β-bromo-substituted derivatives have been observed, the separation of which was effected by chromatographic methods. This makes the use of individual compounds difficult and requires the selection of the optimum conditions for obtaining particular products [3]. The bromination of emodin (I) was first performed in 1888, but the structures of the mono- and dibromoderivatives obtained were not shown [4]. There are no later applications in the literature on the bromination of emodin.

In the present paper we describe the bromination of emodin by dioxane dibromide in CH₃COOH and dioxane solutions, by bromine in acidic (CH₃COOH, H₂SO₄) and organic (C₂H₅OH, CHCl₃, CCl₄, C₆H₆O₂) media, and also in the presence of initiators - benzoyl peroxide and UV light. The emodin/bromine ratio was varied from 1:1 to 1:10 in a temperature regime from 5°C to the
In an acid medium at an equimolar emodin/bromine ratio, on a chromatogram the initial emodin was observed, in addition to the reaction products, and therefore the reaction was subsequently performed in an excess of bromine. Thus, when it was carried out in H₂SO₄, eight bromine derivatives of emodin were detected in the reaction mixture, of which 4-bromo-3-methyl-1,6,8-trihydroxyanthraquinone (II), 5-bromo-3-methyl-1,6,8-trihydroxyanthraquinone (III), 4,5-dibromo-3-methyl-1,6,8-trihydroxyanthraquinone (IV), and 2,4,5,7-tetrabromo-3-methyl-1,6,8-trihydroxyanthraquinone (V) were formed in predominating amounts, products (II-IV) being produced in the course of the first hour and (V) later.

In CH₃COOH at 80°C, likewise, products (II-IV) were obtained, and, on cooling, products (III) and (IV) precipitated, trace amounts of these compounds remaining in the solution together with product (II). The latter was obtained quantitatively by the reaction with dioxane dibromide in an acid solution at 25°C, product (III) being present in the solution in trace amounts. In boiling dioxane, the same two bromides were obtained in a ratio of 7:3.

In organic media, 2-bromo-3-methyl-1,6,8-trihydroxyanthraquinone (IV), 7-bromo-3-methyl-1,6,8-dihydroxyanthraquinone (VII), and 2,7-dibromo-3-methyl-1,6,8-trihydroxyanthraquinone (VIII) were obtained in addition to product (V).

When the conditions of initiation and photobromination at the same temperature of the experiments were compared, it was observed that in the course of 4 h (hv, 250 W) and 2 h