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 methyliodide 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 × 10 ml). The combined extracts were dried over Na_2SO_4. 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].

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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 reactants, 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 CH_3COOH and dioxane solutions, by bromine in acidic (CH_3COOH, H_2SO_4) and organic (C_2H_4OH, $CHCl_3$, CCl_4, $C_4H_8O_2$) 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

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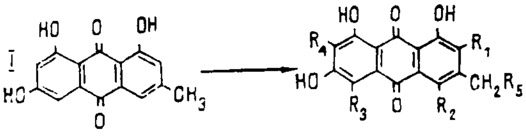
TABLE 1. Physicochemical Properties of Emodin Bromides

Compound	mp, °C	UV, λ_{max}, nm	IR, ν, cm^{-1}			PMR, δ, ppm
			C=O	C–Br	OH	
II	270–272	236,260,288,442, 523	1628,1672	642	3430	6,89 (H-2, s) 7,69 (H-5, d) 7,29 (H-7, d) 2,39 (CH_3, s)
III	218–220	238,266,294,319, 440,520	1626,1670	636	3430	6,88 (H-2, s) 7,65 (H-4, s) 7,27 (H-7, s) 2,38 (CH_3, s)
IV	225–226	238,265,312,318, 454,526	1622,1672	640,676	3420	6,87 (H-2, s) 7,26 (H-7, s) 2,46 (CH_3, s)
V	260 (decomp.)	256,298,330,456, 540	1620,1686	644,676	3443	2,48 (CH_3, s)
VI	262–264	236,263,297,330, 445	1649,1678	662	3400,3395	7,63 (H-4, s) 7,76 (H-5, d) 7,52 (H-7, d) 2,42 (CH_3, s)
VII	228–230	242,268,296,327, 448	1636,1676	645,678	3395,3420	6,80 (H-2, s) 7,60 (H-4, s) 7,78 (H-5, s) 2,44 (CH_3, s)
VIII	238–240	242,269,298,332, 454	1638,1677	648,680	3410,3380	7,64 (H-4, s) 7,77 (H-5, s) 2,38 (CH_3, s)
IX	185–187	290,420	1672,1628	652,671	3440	6,98 (H-2, s) 7,85 (H-4, s) 7,28 (H-5, d) 7,11 (H-7, d) 3,66 (CH_3, s)

boiling point of the solvent over 4 h. The dynamics of the accumulation of the reaction products in time was observed by the TLC method on Silufol plates. The physicochemical properties of the compounds obtained are given in Table 1, and the reaction scheme below:



II. $R_1 = R_3 = R_4 = R_5 = H$; $R_2 = Br$
III. $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = Br$
IV. $R_1 = R_4 = R_6 = H$; $R_2 = R_3 = Br$
V. $R_5 = H$; $R_1 = R_2 = R_3 = R_4 = Br$

VI. $R_2 = R_3 = R_4 = R_5 = H$; $R_1 = Br$
VII. $R_1 = R_2 = R_3 = R_6 = H$; $R_4 = Br$
VIII. $R_2 = R_3 = R_5 = H$; $R_1 = R_4 = Br$
IX. $R_1 = R_2 = R_3 = R_4 = H$; $R_5 = Br$

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 H_2SO_4 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 CH_3COOH 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 (hν, 250 W) and 2 h (benzoyl peroxide) at a ratio of 1:2 the reaction took place selectively with the formation of 3-bromomethyl-1,6,8-trihydroxyanthraquinone (IX).

EXPERIMENTAL

IR spectra were recorded on a Specord 75 IR instrument, PMR spectra on a Bruker MSL-400 instrument in CCl_4, and UV spectra on a UVAS spectrophotometer. Column chromatography was conducted on silica gel L 100/160. The dioxane dibromide was obtained by the procedure of [5]. The results of the elementary analyses of all the compounds corresponded to the calculated figures.

4-Bromo-3-methyl-1,6,8-trihydroxyanthraquinone (II). At 25°C with stirring, 0.125 g ($5 \cdot 10^{-4}$ mole) of dioxane dibromide was added to 0.135 g ($5 \cdot 10^{-4}$ mole) of (I) dissolved in CH_3COOH. The temperature was slowly raised to that of the room [sic]. Product (II) precipitated in the form of yellow crystals, which were filtered off, washed with ether, and dried. Yield, 0.127 g (94%), Found, %: C 51.59; H 2.48; Br 22.85, $C_{15}H_9O_5Br$.

5-Bromo-3-methyl-1,6,8-trihydroxyanthraquinone (III). A. Slowly, dropwise, 0.2 ml ($5 \cdot 10^{-3}$ mole) of Br_2 in 5 ml of H_2SO_4 was added to a solution of 0.135 g ($5 \cdot 10^{-4}$ mole) of (I) in 50 ml of H_2SO_4. The reaction mixture was stirred for 4 h and was poured onto ice, and the precipitate that deposited was filtered off, washed with water to neutrality, and dried. This gave the total bromides, which were separated by adsorption chromatography on silica gel with elution by mixtures of hexane and acetone in ratios of from 10:1 to 1:1. The yield of (II) was 0.025 g (19%); of (III), 0.05 g (38%); of (IV), 0.03 g (22%); and of (V), 0.02 g (14%). Found, %: for (III): C 51.46; H 2.51; Br 22.78. $C_{15}H_9O_5Br$; for (IV) – C 42.12; H 1.89; Br 37.24; $C_{15}H_8O_5Br_2$, and for (V) – C 30.65; H 1.06; Br 56.20, $C_{15}H_6O_5Br_4$.

B. With stirring and heating to 80°C, 0.135 g ($5 \cdot 10^{-4}$ mole) of (I) was dissolved in 50 ml of CH_3COOH. After the (I) had dissolved, 0.2 ml ($5 \cdot 10^{-3}$ mole) of Br_2 in 5 ml of CH_3COOH was added dropwise. The reaction mixture was stirred with continued heating for 4 h. On cooling, an orange precipitate (of (III) and (IV)) precipitated, which was filtered off; the mother solution was poured onto ice and the resulting precipitate consisted of a mixture of (II), (III), and (IV) which was subjected to separation as described in paragraph A. The yield of (II) was 0.04 g (29%); of (III), 0.031 g (23%); and of (IV), 0.064 g (47%).

2,4,5,7-Tetrabromo-3-methyl-1,6,8-Tetrabromo-3-methyl-1,6,8-trihydroxyanthraquinone (V). Crystalline iodine (0.016 g; $6 \cdot 10^{-6}$ mole) was sublimed. With cooling, 0.135 g ($5 \cdot 10^{-4}$ mole) of (I), dissolved in 50 ml of a mixture of absolute C_2H_5OH and CCl_4 in a ratio of 2:3, and 0.2 ml ($5 \cdot 10^{-3}$ mole) of Br_2 were added. The reaction was performed in a sealed tube with heating in a sand bath at a temperature of 170-180°C for 18 h. Then the mixture was poured into ice water, and the orange precipitate that deposited was filtered off and was washed with distilled water. Product (V) was purified by the chromatographic method on a column of silica gel with elution by hexane–acetone (1:1). Yield 0.115 g (85%).

2-Bromo-3-methyl-1,6,8-trihydroxyanthraquinone (IV), 7-Bromo-3-methyl-1,6,8-trihydroxyanthraquinone (VII), and 2,7- Dibromo-3-methyl-1,6,8-trihydroxyanthraquinone (VIII). A reaction flask was charged with 5.0 g ($3 \cdot 10^{-2}$ mole) of sublimed iodine and 1.5 g ($5.5 \cdot 10^{-3}$ mole) of (I) in 80 ml of absolute C_2H_5OH. The mixture was heated for an hour in the presence of 0.85 g ($5 \cdot 10^{-3}$ mole) of $AgNO_3$, and then 2.9 ml ($5.5 \cdot 10^{-2}$ mole) of Br_2 in C_2H_5OH was slowly added dropwise. The reaction was performed at 70-75°C for 14 h. After its end, the mixture was poured onto ice and the precipitate that deposited was filtered off and was washed with distilled water. The material obtained contained (VI), (VII), and (VIII), which were separated on a column of silica gel with elution by toluene–methanol in ratios of from 10:1 to 1:1. The yield of (VI) was 0.51 g (34%); of (VII), 0.4 g (27%); and of (VIII), 0.59 g (39%). Found, %: for (VI) – C 51.36; H 2.25; Br 22.71. $C_{15}H_9O_5Br$, for (VII) – C 51.50; H 2.44; Br 22.88. $C_{15}H_9O_5Br$; and for (VIII) – C 42.06; H 1.88; Br 37.24. $C_{15}H_8O_5Br_2$.

3-Bromomethyl-1,6,8-trihydroxyanthraquinone (IX). A. A solution of 1.5 g ($5.5 \cdot 10^{-3}$ mole) of (I) in dioxane was treated with 0.1 g ($6 \cdot 10^{-4}$ mole) of benzoyl peroxide, and 0.6 ml ($1.1 \cdot 10^{-2}$ mole) of Br_2 was gradually added dropwise. The mixture was heated to the boil during 2 h and it was then cooled and was poured onto ice; the precipitate of (IX) that deposited was filtered off, dried in the air, and was purified by fractional crystallization from dioxane, acetone, and ether. Yield 1.29 g (86%). Found, %: C 51.49; H 2.64; Br 22.85, $C_{15}H_9O_5Br$.

B. In a quartz flask, 1 g ($4 \cdot 10^{-4}$ mole) of (I) was dissolved in dioxane and, with stirring, a solution of 0.4 ml ($8 \cdot 10^{-4}$ mole) of Br_2 in dioxane was added dropwise over 0.5 h. The reaction was performed with illumination by a UV lamp with a power of 250 W at 100°C for 4 h. The solution was worked up in a similar way to experiment A. Yield 81%.

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COMPLEXES OF THE PORPHYRINS OF KARAZHANBASS PETROLEUM WITH TRANSITION-METAL IONS

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The possibility and prospects of the use of petroleum porphyrins isolated from Karazhanbass petroleum for the synthesis of complex compounds of the transition metals has been shown.

Complexes of porphyrins with transition metal ions are effective homogeneous catalysts of a number of chemical processes [1]. The high cost of synthetic porphyrins is dictating the necessity for finding new sources of these substances. One of the possible natural sources is petroleum with a high content of metalloporphyrins.

As has been shown [2, 3] the mineral oils of the Buzachi anticline contains porphyrins in the form of complexes with nickel and vanadyl in concentrations of up to 1 kg per ton and can be considered as a full-value substitute for expensive and poorly available biological porphyrin compounds.

It has been shown previously [3] by the methods of electronic and PMR spectroscopy that the vanadylporphyrins of the Karazhanbass petroleum are represented by a set of homologs relating mainly to two series, M and M-2. The vanadylporphyrins from the Karazhanbass obtained from borehole 851 were isolated by a combined extraction-chromatographic method [4]. To determine the total content of vanadylporphyrin complexes in the petroleum and to extract them completely they were isolated from the petroleum directly by the procedure of Bogomolov et al. [5] with the aid of hot ethanol—acetone extraction. For the quantitative determination of the vanadylporphyrins the optical density of the extract at 572 nm was measured with the aid of a Specord UV-Vis spectrophotometer. Table 1 gives the results of a study of the influence of the selectivity of the solvents on the extraction of the vanadylporphyrins from the oil of the Karazhanbass deposit. The most effective extractant proved to be dimethylformamide (DMFA). Since the petroleum of the Karazhanbass deposit and DMFA have almost identical densities (0.95 g/cm^3), to achieve phase separation we used the preliminary dilution of the petroleum with hexane to decrease its density.

With the aim of detecting homologs of the vanadylporphyrins from the Karazhanbass petroleum we made a mass-spectrometric investigation on a MS-30 instrument at an ionization energy of 70 eV and with the gradual heating of the sample from 50 to 325°C. Analysis of the mass

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