Tetrakis(4-aminophenyl)porphin (II). A) A 6-g (7.6 mmole) sample of I was stirred for 30 min with 300 ml of concentrated HCl, after which 26 g of $SnCl_2 \cdot 2H_2O$ was added, and the mixture was heated rapidly to 80°C and maintained at this temperature for 30 min. It was then cooled and diluted with 300 ml of water, and the precipitated hydrochloride of II was removed by filtration and dissolved in water. The aqueous solution was treated with ammonium hydroxide until the color of the mixture changed. The precipitated II was washed with water, dried, dissolved in chloroform, and chromatographed on silica gel using chloroform as the eluent. Evaporation of the eluate and crystallization of the residue from chloroform–hexane gave 4.74 g (93%) of II.

B) A 0.1-g sample of tetrakis(4-acetamidophenyl)porphin was dissolved by heating in 25 ml of 25% H_2SO_4, and the solution was heated to 70°C for 15 min. It was then cooled, and II was precipitated by the addition of ammonium hydroxide until the color of the mixture changed. The porphin was removed by filtration, washed with water, dried, and recrystallized from chloroform–hexane. The product had R_f 0.71 (methanol) and 0.47 [acetone–heptane (2:1)]. Electronic spectrum in benzene, λ_{max} (log ε): 658 (3.74), 598 (3.61), 563 (4.02), 523 (3.99), 492 (3.61), 421 nm (5.55).

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REACTION OF o-QUINONES OF THE BENZOFURAN AND INDOLE SERIES WITH ACETOACETIC ESTER AND ACETYLACETONE

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The reaction of o-quinones of the benzofuran and indole series with acetoacetic ester and acetylacetone in the presence of zinc chloride leads to derivatives of 4,5-dihydroxybenzofuran and 4,5-dihydroxyindole with acetoacetic ester and acetylacetone residues in the 7 position.

We have found that o-quinones of the benzofuran (I-III) and indole (IV-VI) series, like p-quinones [1, 2], react with keto enols (VII, VIII) in the presence of zinc chloride as the catalyst. However, o-quinones [3, 4] are considerably more reactive. Thus the reaction of keto enols with o-quinones takes place when the reactions are heated in alcohol for 10-15 min. The previously inaccessible 4,5-dihydroxybenzofuran (IX-XIII) and 4,5-dihydroxyindole (XIV-XVII) derivatives (Table 1) with acetoacetic ester and acetylacetone residues in the 7 position are formed in high yields as a result of this reaction.

Thus we proposed a new preparative method for the dihydroxyheterylation of keto enols.

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TABLE 1. Derivatives of 4,5-Dihydroxybenzofuran (IX-XIII) and 4,5-Dihydroxyindole (XIV-XVII)

Compound	R	R¹	Hal	X	mp,[a] °C	Found, %			Empirical formula	Calc., %			Yield, %
						C	H	Hal		C	H	Hal	
IX	CH_3	OC_2H_5	Cl	O	170—172	54,3	4,7	8,8	$C_{18}H_{19}ClO_8$	54,2	4,8	8,9	80
X	CH_3	CH_3	Cl	O	190—191	55,5	4,6	9,4	$C_{17}H_{17}ClO_7$	55,4	4,6	9,6	86
XI	CH_3	OC_2H_5	Br	O	178—180	48,9	4,4	18,1	$C_{18}H_{19}BrO_8$	48,8	4,3	18,0	77
XII	CH_3	CH_3	Br	O	203—205	49,5	4,1	19,2	$C_{17}H_{17}BrO_7$	49,4	4,1	19,3	79
XIII	C_6H_5	OC_2H_5	Br	O	140—142	54,8	4,5	15,7	$C_{23}H_{21}BrO_8$	54,7	4,2	15,8	73
XIV	CH_3	OC_2H_5	Br	NC_6H_5	203—204	55,4	4,5	15,6	$C_{24}H_{24}BrNO_7$[b]	55,6	4,7	15,4	72
XV	CH_3	OC_2H_5	Br	$NC_6H_4CH_3$-4	218—220	56,4	5,1	14,8	$C_{25}H_{26}BrNO_7$[c]	56,4	4,9	15,0	85
XVI	CH_3	CH_3	Br	$NC_6H_4CH_3$-4	195—196	57,0	5,0	16,3	$C_{24}H_{24}BrNO_6$[d]	57,4	4,8	15,9	71
XVII	CH_3	OC_2H_5	Br	$NC_6H_4OCH_3$-4	202—203	54,8	4,6	14,3	$C_{25}H_{26}BrNO_8$[e]	54,7	4,8	14,6	78

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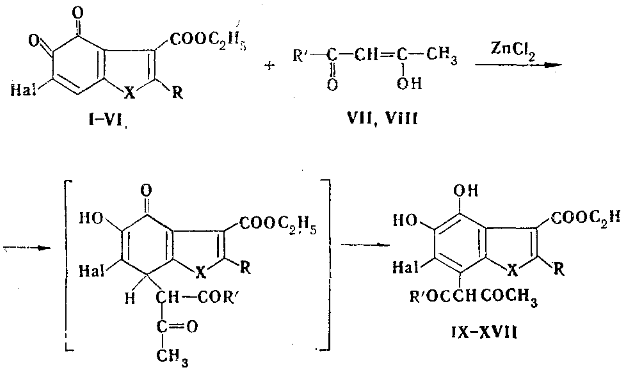
[a] The compounds were crystallized: IX and XV from benzene, X-XIV and XVI from alcohol, and XVII from acetic acid. [b] Found: N 2.5%. Calculated: N 2.7%. [c] Found: N 2.5%. Calculated: N 2.6%. [d] Found: N 2.5%. Calculated: N 2.8%. [e] Found: N 2.7%. Calculated: N 2.5%.

TABLE 2. Spectral Characteristics of IX-XVII

Compound	IR spectrum, cm⁻¹		UV spectrum, λ_{max}, nm (log ε)
	C=O	OH	
IX	1665, 1640, 1620	3440	218 (4,26); 250 (4,0); 310 (3,38)
X	1660, 1610, 1585	3540	218 (4,60); 255 (4,22)
XI	1660, 1640, 1620	3440	218 (4,63); 250 (4,35); 310 (3,62)
XII	1660, 1610, 1580	3530	218 (4,62); 257 (4,22)
XIII	1650, 1590, 1580	3480	220 (4,63); 250 (4,36); 320 (4,08)
XIV	1630, 1600, 1590	3445	223 (4,62); 260 (4,34); 320 (3,65)
XV	1655, 1635, 1620	3500	260 (4,42); 320 (3,92)
XVI	1640, 1610	3350	225 (4,73); 264 (4,38); 305 (4,05)
XVII	1640, 1580	3440	225 (4,68); 264 (4,47); 320 (4,00)



I R=CH_3, Hal=Cl, X=O; II R=CH_3, Hal=Br, X=O; III R=C_6H_5, Hal=Br, X=O; IV R=CH_3, Hal=Br, X=N—C_6H_5; V R=CH_3, Hal=Br, X=N—$C_6H_4CH_3$-4; IV R=CH_3, Hal=Br, X=N—$C_6H_4OCH_3$-4; VII R¹=OC_2H_5; VIII R¹=CH_3

The structures of IX-XVII were proved by the presence in their IR spectra of the intense absorption band that is characteristic for the OH group at 3350-3530 cm⁻¹, as well as by an absorption band at 1580-1665 cm⁻¹, which indicates the presence of ester and carbonyl groups belonging to a "keto enol" substituent (Table 2).

The mass numbers of the molecular ions found in the mass spectra of IX-XVII are in agreement with the calculated values.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with UR-10 and Perkin-Elmer spectrometers. The UV spectra of solutions in alcohol were recorded with Hitachi EPS-3T and Perkin-Elmer 575 spectrometers. The mass spectra were recorded with a Varian MAT-

112 mass spectrometer (70 eV) with direct introduction of the samples into the ion source. The individuality of the substances was monitored on Silufol UV-254 plates in chloroform with development in UV light.

2-Methyl-3-ethoxycarbonyl-4,5-dihydroxy-6-chloro-7-(1'-ethoxycarbonyl-2'-oxopropyl)benzofuran (IX). A mixture of 13.4 g (0.05 mole) of 2-methyl-3-ethoxycarbonyl-4,5-dioxo-4,5-dihydro-6-chlorobenzofuran (I), 28g (0.1 mole) of acetoacetic ester (VII), and 26 g (0.1 mole) of anhydrous zinc chloride in 500 ml of absolute ethanol was refluxed with stirring for 15 min, after which the solution was cooled to 40°C and treated with 20 ml of a solution of $Na_2S_2O_4$ and 250 ml of water to decolorize the colored impurities. The resulting precipitate was removed by filtration, washed with water, and dried to give 16 g (80%) of product. Compounds X-XVII (Table 1) were obtained by a similar method.

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SYNTHESIS OF INDENOINDOLES ON THE BASIS OF 2-AMINOFLUORENE AND 2-AMINOFLUORENONE

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Ethyl esters of 2-carboxylic acids of 3H,10H-indeno[2,1-e]-1H,9H-indeno[1,2-f]indoles and their keto derivatives were obtained on the basis of 2-aminofluorene and its 9-keto derivative via the Japp—Klingemann and Fischer reactions. Saponification with subsequent decarboxylation of these products leads to unsubstituted cyclic systems and their keto derivatives.

Despite the large volume of research devoted to the synthesis and study of the properties of new heterocyclic systems that contain an indole fragment, only several derivatives of 3H,10H-indeno[2,1-e]- and 1H,9H-indeno[1,2-f]indoles have been described in the literature [1, 2]. In the present research we made an attempt to synthesize these compounds on the basis of the readily accessible fluorene derivatives 2-aminofluorene and 2-aminofluorenone via the scheme presented below.

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