TABLE 1. Constants of 3-Carbalkoxy-4-(1,2-epoxypropyl)-Δ^2-pyrazolines (VIa-c)

Compound	R	mp, °C	Found, %			Empirical formula	Calc., %			UV spectrum, λ_{max}, nm (log ε)	Yield, %
			C	H	N		C	H	N		
VIa	CH_3	62—63	53,5	6,5	15,0	$C_8H_{12}N_2O_3$	52,2	6,5	15,2	300 (4,00)	45
VIb	C_2H_5	116—117	54,6	7,2	13,9	$C_9H_{14}N_2O_3$	54,5	7,1	14,1	298 (4,04)	80
VIc	C_3H_7	91—92	56,0	5,8	13,0	$C_{10}H_{16}N_2O_3$	56,6	6,5	13,2	300 (4,04)	48

3-Carbalkoxy-4-(1,2-epoxypropyl)-Δ^2-pyrazolines (VIa-c). A 10-g (0.07 mole) sample of 4,5-epoxy-2-hexenoic acid ester was added with stirring to an ether solution of 0.14 mole of diazomethane obtained from nitrosomethylurea, and the solution was maintained at 0-5°C for 48 h. The precipitated crystals were recrystallized from alcohol. The constants of the corresponding pyrazolines are presented in Table 1.

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POLAROGRAPHY OF FURAN-2-CARBOXYLIC ACID ESTERS

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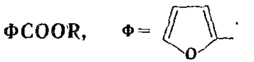
UDC 547.725'26:543.253

The polarographic reduction of furan-2-carboxylic acid esters in dimethylformamide was studied. The $E_{1/2}$ values correlate with the σ* constants for the substituents in the alcohol part of the 2-furoates.

We have previously shown that the electrophilicity of the carbonyl group of furan-2-carboxylic acid esters in processes involving the formation of an intermolecular hydrogen bond depends on the character of the substituent in both the 5 position of the furan ring and in the alcohol part of the molecule [1, 2]. It is also known that the rate-determining step in nucleophilic substitution reactions of the $B_{Ac}2$ type is attack by the nucleophile at the carbonyl carbon atom [3]. In this connection it is of interest to evaluate the electron-acceptor capacity of the C=O group by polarography.

The results of polarographic reduction in dimethylformamide (DMF) of some furan-2-carboxylic acid esters are presented in this paper.



$R = CH_3, C_2H_5, C_3H_7, C_4H_9, CH_2{-}CH{=}CH_2, CH_2{-}C{\equiv}CH; CH_2{-}C_6H_5, CH_2{-}\Phi$

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*Deceased.

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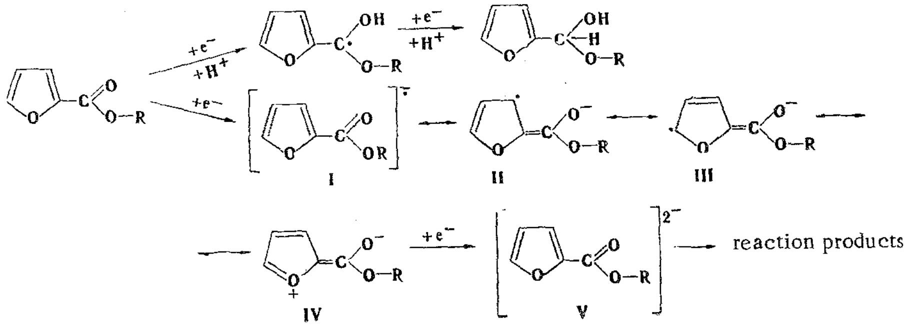
Under the investigated conditions furoates form a complex irreversible two-electron diffusion wave. In a study of the effect of the depolarizer concentration on the heights of the polarographic waves it was ascertained that the dependence $i_{lim} = f(c_{dep})$ for all of the investigated 2-furoates is rectilinear in character, while the temperature coefficients of propyl, allyl, and propargyl 2-furoates range from 1.6 to 1.9%; this may serve as a confirmation of the diffusion nature of the waves [4].

It is known that in aqueous solutions the course of the reduction of carbonyl compounds depends on the pH: in acidic media they give two one-electron waves, whereas when the pH is increased, the first wave is shifted to the more negative region and merges with the second wave when pH > 6 [5]. In aqueous alcohol media with a lithium acetate buffer as the inert electrolyte at pH 6.7 the reduction of vinyl 2-furoates is also limited by the formation of the hemiacetal; the successive addition of both electrons with simultaneous protonation of the products of stepwise reduction of the carbonyl group is assumed in this case. The rate of the second step is considerably higher than that of the first, and one two-electron wave is therefore observed on the polarogram. The furan ring and the vinyl group remain unaffectec [6]. However, protonation of the anion radical formed in the first step is hindered in an aprotic medium. The participation of the bonds of the furan ring is also possible in this case during reduction of the depolarizer to dianion V:



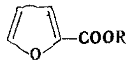
The participation of the furan ring in stabilization of the anion radical was also assumed in a study of the electrochemical reduction of 5-nitrofurans in DMF [5], while the possibility of realization of a structure of the IV type is also provided for in the electrolytic reduction of compounds with a pyran ring [7]. In connection with the fact that adsorption processes are insignificant in organic media, the form of the dependences of log $[i/(i_{lim} - i)]$ on E for the 2-furoates that we investigated may serve as a confirmation of the two-step character of the process, and the two-electron wave observed in the polarogram is the sum of two one-electron waves with close $E_{1/2}$ values that are not separated under the polarographic conditions. In contrast to this, the clearly expressed two-wave reduction of benzoates in anhydrous DMF [8] can be explained by the considerably greater ability of the phenyl ring to stabilize the anion radical formed in the first step of the reduction.

It is apparent from Table 1 that lengthening the alkyl chain shifts $E_{1/2}$ to the more negative region, which corresponds to an incrase in the positive inductive effect of alkyl groups on the electron-deficient reaction center. Correlation treatment of the dependence of $E_{1/2}$ on the Taft inductive constants of the alkyl radicals of the alkoxy groups of 2-furoates $\Phi COOCH_2R$ under the investigated conditions led to a linear equation (method of least squares, P = 0.95, n = 8). Since the σ* values presented in literature sources for the furyl radical display substantial differences (0.36 [9]; 1.08 [10]; 0.7, 1.17, 0.96, 1.24 [11]), we used the average of the last five values, viz., $\sigma^*_\Phi = 1.01 \pm 0.35$, for the correlation.

$$E_{1/2} = (-2.38 \pm 0.04) + (0.19 \pm 0.03)\sigma^*_{CH_2X}, \quad r = 0.97$$

In this equation the reaction sensitivity constant is relatively small and virtually coincides with the constant of the analogous equation that links the half-wave potential for the reduction of 2-furoates with the Taft inductive constants of the alkoxy groups also in the case of polarography in aqueous alcohol media [12]. On the basis of this, it may be concluded that alkoxy groups have a slight and identical effect on the reduction of 2-furoates in both protic and aprotic media.

TABLE 1. Data on the Polarographic Reduction of Furan-2-carboxylic Acid Esters in DMF



R	$-E_{1/2}$, V, relative to a saturated calomel electrode	n
CH_3	2,35	2,12
CH_2CH_3	2,40	1,91
$CH_2CH_2CH_3$	2,42	1,92
$CH_2CH_2CH_2CH_3$	2,43	1,97
$CH_2—CH{=}CH_2$	2,32	2,30
$CH_2—C{\equiv}CH$	2,13	1,79
$CH_2—C_6H_5$	2,22	1,81
$CH_2—\Phi$	2,18	2,04

A tendency for facilitation of the reduction of furoates with more unsaturated alkoxy groups in conformity with the change in their negative inductive effect is noted when one compares the $E_{1/2}$ values of propyl, allyl, and propargyl esters of furan-2-carboxylic acid.

It is known that the furan ring in processes involving the reduction of an electrically active substituent can be characterized by both positive and negative electronic effects with respect to the phenyl ring [6, 10, 13]. The data in Table 1 demonstrate graphically that with respect to their electron-acceptor effect on the reaction center under the conditions that we investigated the furyl and phenyl groups occupy an intermediate position between vinyl and ethynyl groups, whereas the furyl ring in turn has a greater electron-acceptor effect than the phenyl group.

Thus our results make it possible to quantitatively evaluate the electron-acceptor capacity of carbonyl groups in a series of furan-2-carboxylic acid esters as a function of their structure.

EXPERIMENTAL

Polarography was carried out in a thermostatted cell at 25°C with an LP-7 polarograph with a dropping mercury electrode. The half-wave potentials were measured relative to a saturated calomel electrode. The sensitivity of the recorder was 50 μA. The capillary characteristics were $m = 0.836$ mg/sec and $t = 0.334$ sec^{-1} when $E = -1.00$ V. The concentration of the ester solutions was 10^{-3} M, and the concentration of the $(C_2H_5)_4NI$ inert electrolyte was $5 \cdot 10^{-2}$ M. The dimethylformamide (GOST 20289–74 chemically pure) was additionally purified by prolonged storage over KOH and fractionation over CaO. The middle third of the distillate was selected. Prior to use, the tetraethylammonium iodide was additionally dried in vacuo at 50°C for 10 h. The purity of the investigated esters was monitored by gas–liquid chromatography.

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SYNTHESIS OF 2,3-DIFORMYL-5-ETHYLBENZOFURAN AND ITS DERIVATIVES

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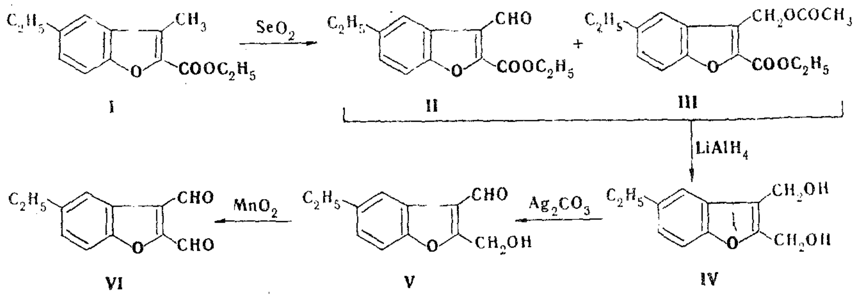
A mixture of 3-formyl and 3-acetoxymethyl derivatives is formed in the oxidation of 2-carbethoxy-3-methyl-5-ethylbenzofuran with selenium dioxide. Reduction of the products with lithium aluminum hydride gives the corresponding 2,3-dihydroxymethyl derivatives, which are converted to 2,3-diformyl derivatives by successive oxidation by the Fetizon method and with manganese dioxide. The corresponding benzofuro[2,3-d]pyridazines were synthesized by reaction of 2-carbethoxy-3-formyl-5-ethylbenzofuran with hydrazine hydrate.

The biological activity of many benzofuran derivatives has been the subject of intensive investigation [1-3]. In a continuation of previous research on benzofuran derivatives [4, 5], the present study is devoted to the synthesis of previously undescribed diformyl derivatives of 2-carbethoxybenzofuran.

The starting 2-carbethoxy-3-methyl-5-ethylbenzofuran (I) was obtained from p-ethylphenol by the Boheme method [6]. Oxidation of this compound with selenium dioxide in glacial acetic acid led to 2-carbethoxy-3-formyl-5-ethylbenzofuran (II) and 2-carbethoxy-3-acetoxymethyl-5-ethylbenzofuran (III). 2,3-Dihydroxymethyl-5-ethylbenzofuran (IV) was obtained by the action of lithium aluminum hydride on II and III. We then carried out the direct oxidation of IV by means of SeO_2, MnO_2, and CrO_3 in order to obtain 2,3-diformyl-5-ethylbenzofuran. However, numerous attempts did not give positive results. Only the unchanged starting compound and a small amount of resinous substances were obtained each time. The reaction was then carried out in two steps. Compound IV was initially subjected to oxidation with Ag_2CO_3 by the method of Fetizon and Goldfier [7], and the resulting 2-hydroxymethyl-3-formyl-5-ethylbenzofuran (V) was oxidized with active MnO_2 to give 2,3-diformyl-5-ethylbenzofuran (VI). The results of analysis of the compounds thus obtained by PMR spectroscopy confirmed the indicated course of the reaction.



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