

Tetronic acid in Reaction with Aromatic Aldehydes and 2-Naphthylamine. Investigation of Fluorescent and Nonlinear-Optical Characteristics of Compounds Obtained

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Abstract—By Knoevenagel condensation and by three-component condensation 3-arylmethylenetetrahydrofuran-2,4-diones and previously unknown 8,11-dihydro-11-arylbenzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-ones were respectively synthesized. The luminescent spectra and nonlinear-optical characteristics of compounds obtained were investigated.

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Tetrahydrofuran-2,4-dione (**I**) widely known as β -tetronic acid is a promising convenient building block for the synthesis of structures of lignan type that attract a constant scientific and practical interest as components of a group of naturally occurring compounds [1–3] and as organic luminophors with fused five- and six-membered heterocycles [4]. In the series of these compounds azaanalogs exist of lignan structures whose synthesis occurs in two stages. The first stage consists in the preparation of 3-arylmethylenefurandiones, the second one, in their condensation with aromatic amines.

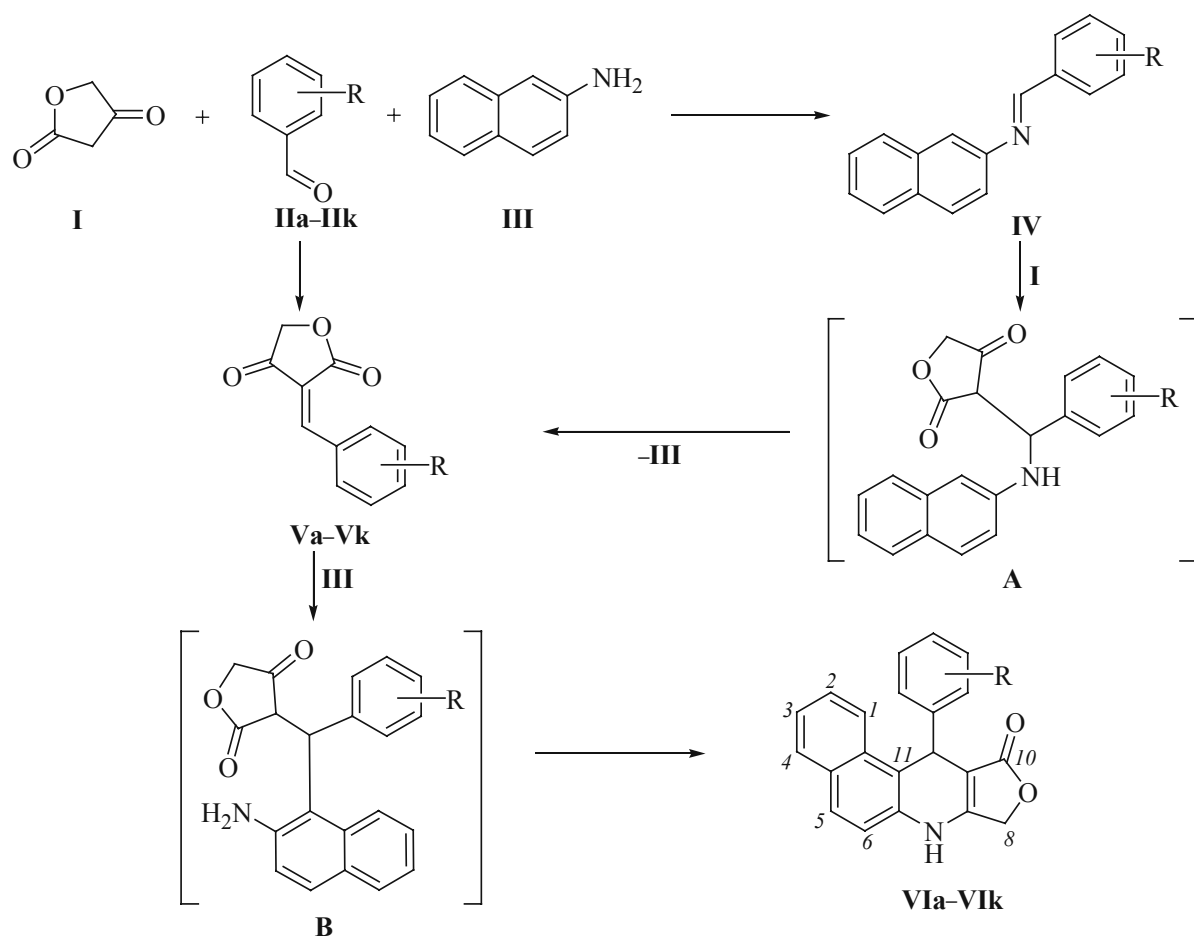
The target of the present study was the preparation of 3-arylmethylenetetrahydrofuran-2,4-diones **Va–Vk** proceeding from tetronic acid (**I**) and aromatic aldehydes **IIa–IIIk**, the reaction of compounds **Va–Vk** with 2-naphthylamine (**III**) and the three-component condensation involving tetronic acid, aromatic aldehydes and 2-naphthylamine, and the investigation of luminescent spectra and nonlinear-optical characteristics of compounds obtained.

The Knoevenagel condensation of equimolar quantities of tetronic acid (**I**) and aromatic aldehydes **IIa–IIIk** by heating the reagents mixture in alcohol led to the formation in preparative amounts of the target 3-arylmethylenetetrahydrofuran-2,4-diones **Va–Vk**. In this reaction the formation of the cross-conjugated multiple bond

is catalyzed by the proton of the enolyzed β -dicarbonyl compound **I**.

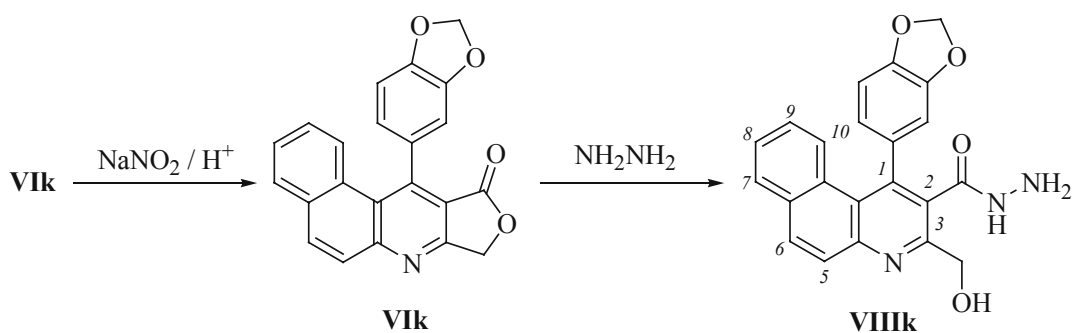
By boiling of compounds **Va–Vk** with 2-naphthylamine in alcohol solution for 20–40 min we obtained 8,11-dihydro-11-arylbenzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-ones **VIa–VIk**. The same compounds we synthesized by a three-component condensation of tetrahydrofuran-2,4-dione (**I**), aromatic aldehydes **IIa–IIIk**, and 2-naphthylamine (**III**) at the simultaneous charge of all components or by boiling in alcohol of two of these components followed by adding the third one after 15 min without isolation of intermediate reaction products. The boiling of the tetrahydrofuran-2,4-dione with an aromatic aldehyde with subsequent charging 2-naphthylamine into the reaction mixture or boiling the 2-naphthylamine with aldehyde followed by addition of the tetronic acid led to the formation of 8,11-dihydro-11-arylbenzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-ones **VIa–VIk**. The formation of the same reaction products at the different order of reagents charging suggests that the formation of benzo[*f*]furoquinolines occurs both via azomethines of 2-naphthylamine series **IV** (as has been already reported in [5, 6]) and through cross-conjugated tetrahydrofuran-2,4-diones **V**. In the second event unstable iminium intermediate **A** decomposes into 3-arylidenetetrahydrofuran-2,4-dione **V** and 2-naphthylamine. The latter again enters into the addition reaction

Scheme 1.



R = H (a), Cl (b), Br (c), OH (d), OCH₃ (e), N(CH₃)₂ (f), N(C₂H₅)₂ (g), 3,4-(OCH₃)₂ (h), 3-OCH₃-4-one (i), 3-OC₂H₅-4-one (j), 3,4-OCH₂O (k).

Scheme 2.



with β -dicarbonyl compound **V** at the carbon atom in the α -position to the amino group. The heterocyclization of the arising intermediate compound **B** results in compounds **VIa-VIi** (Scheme 1).

The intramolecular cyclization of aminoketone **B** involves exclusively the ketone carbonyl of the tetronic

acid fragment, and in the structure of the final condensation products **VIa-VIi** the lactone moiety is conserved remaining available for further modification of the compounds.

On oxidation of compound **Vk** with sodium nitrite in acetic acid we obtained benzo[*f*]furo[3,4-*b*]quinolin-

10(8*H*)-one (**VIIIk**), whose lactone ring at treating with hydrazine in alcoholic solution opened virtually quantitatively to yield the corresponding hydrazide of 1,3-disubstituted benzo[*f*]quinoline-2-carboxylic acid **VIIIk** (Scheme 2). Hence this sequence of transformations can be an efficient and convenient method of preparation of 1,2,3-substituted derivatives of benzo[*f*]quinoline.

The composition and structure of obtained compounds **Vi**, **Vj**, **VIa–VIk**, **VIIIk**, and **VIIIk** were confirmed by elemental analyses, ¹H NMR and IR spectra.

¹H NMR spectra of compounds **Vi** and **Vj** contain two characteristic singlets of methylene protons of the heterocycle in the region 4.60–4.65 and 4.85–4.90 ppm due to the presence of *E*- and *Z*-geometric isomers in the ratio 2:3. In ¹H NMR spectra of compounds **VIa–VIk** singlets characteristic of these structures are observed from the protons H^{II} and NH at 5.43–5.69 and 9.89–10.31 ppm respectively [7]. The signal from the protons of CH₂OCO group appeared in the spectrum as a doublet of doublets at 4.72–4.95 ppm. The chemical shifts and multiplicity of these signals unambiguously confirm the structure of compounds **VIa–VIk**. ¹H NMR spectrum of oxidation product **VIIIk** lacks the signal from NH group evidencing the complete dehydrogenation. In the ¹H NMR spectrum of hydrazide **VIIIk** a singlet of the alcoholic hydroxy group appears at 9.27 ppm. The protons at the nitrogen atoms give rise to two characteristic multiplet in the region 4.60–4.82 (2H) and 4.95–5.30 (1H) ppm.

In the IR spectra of 3-arylmethylenetetrahydrofuran-2,4-diones **Vi** and **Vj** absorption bands are present of the stretching vibrations of the keto and lactone carbonyls in the range 1740–1730 cm⁻¹ and of the double bond conjugated with them in the region 1635–1640 cm⁻¹. The IR spectra of compounds **VIa–VIk**, and **VIIIk** contain the bands of stretching vibrations of the lactone carbonyl at 1720–1745 cm⁻¹ and of a conjugated double bond in the region 1640–1670 cm⁻¹. The band of the secondary amino group is observed in the range 3330–3180 cm⁻¹ in the spectra of compounds **VIa–VIk**. IR spectrum of compound **VIb** is characterized by the absorption band at 854 cm⁻¹ belonging to C–Cl bond, of compound **VIc**, by the strong band at 562 cm⁻¹ characteristic of the stretching vibrations of the C–Br bond. A strong absorption band in the region 2850–2830 cm⁻¹ belonging to vibrations of OCH₃ group is present in the spectra of compounds **Vi**, **VIe**, **VIh**, and **VIIi**. The absorption band of the stretching vibrations of the hydroxy group at 3400–

3240 cm⁻¹ appears in the spectra of compounds **Vi**, **Vj**, **VId**, **VIIi**, **VIj**, and **VIIIk**.

The comparison of yields of compounds **VIa–VIk** reported in EXPERIMENTAL permits the establishment of some trends in the condensation. The electrophilic groups in the *para*-position of the benzene ring of arylmethylenefurandiones **Vb** and **Vc** decrease the electron density on the exocyclic carbon of the double bond facilitating the addition of 2-naphthylamine, and thus the yield of compounds **Vb** and **Vc** reaches 82 and 84%. The nucleophilic substituent in the benzene rings of arylidenefurandiones **Vd–Vg** through the π -conjugation with the double bond increase the electron density on the reaction site of compounds **V** and hamper the formation of the new C–C bond. Therefore the yield of compounds **VId–VIg** does not exceed 58%. The yield of the reaction products is favored by nucleophilic substituents in the *meta*-position of the benzene ring of disubstituted aldehydes when the second nucleophilic substituent is located in the *para*-position. Yields of 8,11-dihydro-11-(4-hydroxy-3-methoxyphenyl)- (**VIIi**) and 8,11-dihydro-11-(4-hydroxy-3-ethoxyphenyl)- (**VIj**) - benzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-ones equal respectively 82 and 78% and are by 30% higher than the yield of 8,11-dihydro-11-(4-hydroxyphenyl)benzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-one (**VId**), for the presence of the substituents in the *meta*-position reduces the donor effect of the hydroxy group due to the distortion of the coplanarity of dione **V** molecule [8].

The effect of the character of substituent in the benzene ring of aromatic aldehydes on the position of the absorption bands in the electronic spectra (λ_{\max}) and their relative intensity is also revealed in the electronic spectra recorded from ethanol solutions at room temperature. The spectral data are presented in the table and on Figs. 1 and 2. The spectra of dihydrobenzofuroquinolinones **VIc**, **VIg**, **VIh**, **VIj**, and **VIk** are characterized mainly by a system of three electron-vibronic bands located respectively in the ranges 300–380, 250–300, and 200–250 nm (see the table and Fig. 1), they possess a pronounced vibronic structure, and the strongest band is that in the short-wave region with $\lambda_{\max} \sim 220$ nm. 3-Arylmethylenetetrahydrofuran-2,4-diones **Va**, **Vf**, **Vg**, and **Vh** are characterized by absorption spectra displaced into the long-wave region compared to those of compounds **VI**. The most longwave bands are observed in the spectra of compounds **Vg** and **Vf** with λ_{\max} 483 and 480 nm respectively (see the table and Fig. 1). The red shift of the long-wave absorption bands in the series of compounds **Va** (335 nm), **Vh** (385 nm), **Vf** (480 nm), and **Vg**

Spectral and luminescence properties of compounds **Va**, **Vf**, **Vg**, **Vh** and **Vlc**, **Vlg**, **Vlh**, **Vlj**, **VI k** in ethanol solution and polycrystals at room temperature^a

Compound no.	Absorption λ_{\max} , nm (ϵ)	Fluorescence λ_{\max} , nm	
	ethanol	ethanol	polycrystals
Va	335 (0.21), 235 (1.0)	383 w	410 m
Vf	480 (1.0), 248 (0.46), 226 (0.57)	520 w	692 m
Vg	483 (1.0), 258 (0.16), 233 (0.14)	513 w	648 s
Vh	385 (1.0), 248 (0.46)	394 w	415, 558 m
Vlc	350 (0.08), 326 (0.13), 283 (0.39), 224 (1.0)	381 m	449 s
Vlg	483 (1.0), 258 (0.16), 233 (0.14)	513 w	648 s
Vlh	350 (0.08), 325 (0.13), 283 (0.37), 224 (1.0)	380 m	406 s
Vlj	350 (0.09), 325 (0.15), 281 (0.41), 223 (1.0)	381 m	395 s
VIk	350 (0.09), 325 (0.15), 282 (0.41), 225(1.0)	380 m	409 s

^a All compounds under study in the crystalline state at room temperature exhibit fluorescence of various intensity. The registration of fluorescence spectra of compounds **Vf** and **Vg** was performed at λ_{excit} 460 nm, and of all the other compounds, at λ_{excit} 340 nm. Intense fluorescence (s) is characteristic of compounds **Vg**, **Vlc**, **Vlg**, **Vlh**, **Vlj**, **VI k**. The other compounds possess medium (m) intensity of fluorescence. Maxima of the fluorescence spectra vary in a wide spectral range. Whereas for the majority of polycrystals the fluorescence maxima lie about 410 nm, compounds **Vf** and **Vg** fluoresce in the long-wave region at 645 and 692 nm (Fig. 2).

(483 nm) is apparently caused by increased interaction with charge transfer between electron-donor groups OCH_3 , $\text{N}(\text{CH}_3)_2$, $\text{N}(\text{CH}_5)_2$ and the electron-acceptor furandiones [9]. As a result of the increased interaction with the charge transfer in the spectra of compounds **Vf**–**Vh** the intensity of the long-wave absorption bands is stronger than the intensity of the short-wave bands in the range 220–240 nm (see the table). In the spectrum of compound **Va** lacking electron-donor substituents the intensity of the band at 235 nm is 5 times higher than that of the long-wave band at 335 nm.

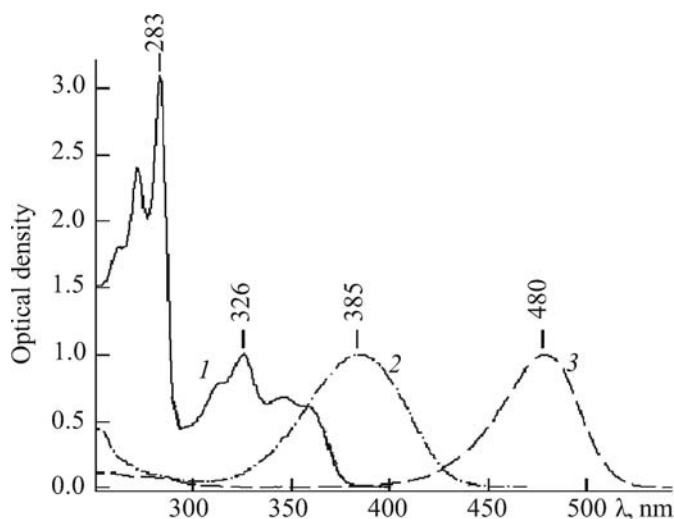


Fig. 1. Electron absorption spectra registered at 293K in ethanol of compounds (1) **VIc**, (2) **Vh**, (3) **Vf**.

8,11-Dihydro-11-(arylphenyl)benzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-ones **Vlc**, **Vlg**, **Vlh**, **Vlj**, **VI k** in ethanol solution at room temperature and λ_{excit} 340 nm exhibit medium intensity fluorescence with the maximum in the region 380–390 nm (see the table). The fluorescence of weak intensity is also characteristic of furandione type compounds in ethanol solution, and the spectral maxima of compounds **Vf** and **Vg** (λ_{excit} 460 nm) are strongly displaced to the long-wave region compared to the spectra of compounds from the benzofuroquinoline series **Vlc**, **Vlg**, **Vlh**, **Vlj**, **VI k** (see the table and Fig. 2).

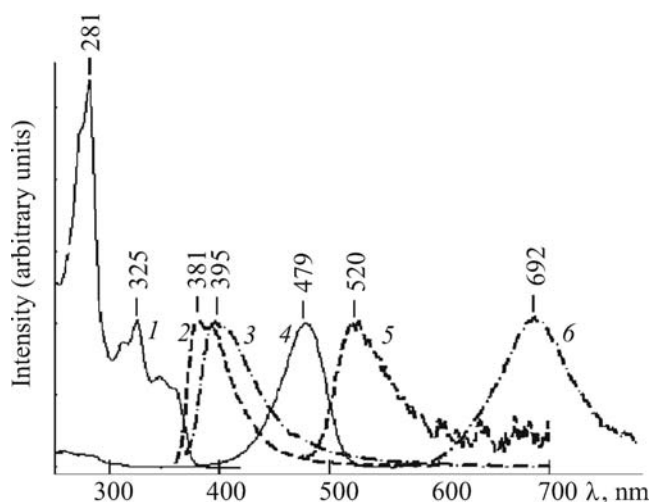


Fig. 2. Absorption (1, 4) and fluorescence (2, 3, 5, 6) spectra of compounds **Vlj** (1–3) and **Vf** (4–6) in ethanol (1, 2, 4, 5) and polycrystals (3, 6) at 293 K.

Compounds **Vf** and **Vg** in the polycrystalline state possess nonlinear-optical properties, namely, they are capable of transforming the frequency of a laser radiation. At excitation with the first harmonic of the radiation of neodymium laser YAG–Nd³⁺ (λ_{excit} 1.06 μm , E_{excit} 80 mJ, pulse length 20 ns) of these polycrystalline compounds a bright red fluorescence, λ_{max} ~640 nm (**Vg**), and dark-red fluorescence, λ_{max} ~690 nm (**Vf**) was observed. This fluorescence arises as a result of simultaneous absorption of two photons (λ 1.06 m) and is two-photon excited.

The discovered nonlinear-optical effect of two-photon excitation for compounds **Vf** and **Vg** suggests them as promising materials for designing elements for visualization of the invisible radiation of IR lasers.

EXPERIMENTAL

Electron absorption spectra were registered at room temperature on a spectrophotometer Cary-500 (Varian, USA). Fluorescence spectra were measured on a spectrofluorimeter SFL-1211A (SOLAR, Belarus'). The two-photon excitation was performed with the use of the first harmonic of the radiation of neodymium laser YAG–Nd³⁺, wave length 1.06 μm . IR spectra were recorded on a Fourier spectrophotometer Nicolet Protégé-460 from thin films or pellets with KBr. NMR spectra were obtained on a spectrometer Bruker AC-500 [500 (¹H), 125 MHz (¹³C)] using 5% solutions in DMSO-*d*₆, chemical shifts measured from an internal reference TMS.

Tetrahydrofuran-2,4-dione (tetronic acid) was prepared along procedure [10] by bromination of ethyl acetoacetate followed by rearrangement of the α -bromide obtained into a γ -isomer under the effect of air oxygen and cyclization of the γ -isomer under the treatment with aqueous alkali.

3-Arylmethylenetetrahydrofuran-2,4-diones Va–Vk were obtained by boiling in alcohol equimolar amounts of tetronic acid (**I**) and an appropriate aldehyde **IIa–IIIk** for 20–30 min. Physicochemical constants of β -dicarbonyl compounds **Va–Vh**, and **Vk** coincide with the published data [11, 12], the parameters of new compounds **Vi** and **Vj** are given below.

(E,Z)-3-(4-Hydroxy-3-methoxybenzylidene)-tetrahydrofuran-2,4-dione (Vi). Yield 71%, yellow crystals. IR spectrum, cm^{-1} : 3400, 3010, 2920, 2830, 1740, 1682, 1640, 1523, 1481, 1320, 1306, 1225, 1100. ¹H NMR spectrum, δ , ppm: 3.93 s (3H, OMe), 4.60 s (2H, CH₂, *E*-isomer), 4.85 s (2H, CH₂, *Z*-isomer), 7.02 m

(2H_{arom}), 7.90 m (1H, C=CH), 8.52 m (1H_{arom}). Found, %: C 59.47; H 4.51. C₁₂H₁₀O₅. Calculated, %: C 59.46; H 4.50.

(E,Z)-3-(4-Hydroxy-3-ethoxybenzylidene)-tetrahydrofuran-2,4-dione (Vj). Yield 62%, yellow crystals. IR spectrum, cm^{-1} : 3387, 3008, 2943, 1730, 1703, 1664, 1635, 1527, 1482, 1317, 1302, 1219, 1113. ¹H NMR spectrum, δ , ppm: 3.95 s (3H, OMe), 4.65 s (2H, CH₂, *E*-isomer), 4.90 s (2H, CH₂, *Z*-isomer), 7.06 m (2H_{arom}), 7.87 m (1H, C=CH), 8.55 m (1H_{arom}). Found, %: C 62.89; H 4.82. C₁₃H₁₂O₅. Calculated, %: C 62.90; H 4.83.

8,11-Dihydro-11-arylbenzo[f]furo[3,4-*b*]-quinolin-10(7H)-ones VIa–VIk. *a*. A solution of 1.43 g (0.01 mol) of 2-naphthylamine (**III**), 0.01 mol of an appropriate aromatic aldehyde **IIa–IIIk**, and 1.3 g (0.01 mol) of tetronic acid (**I**) in 20 ml of ethanol was boiled till the beginning of crystals precipitation (30–60 min). On cooling the separated precipitate was filtered off, washed with ether, and recrystallized from a mixture ethanol–benzene, 1:1.

b. A solution of 1.43 g (0.01 mol) of 2-naphthylamine (**III**), 0.01 mol of an appropriate aromatic aldehyde **IIa–IIIk** in 20 ml of ethanol or a solution of 0.01 mol of aldehyde **IIa–IIIk** and 1.3 g (0.01 mol) of tetronic acid (**I**) in 20 ml of ethanol was boiled for 15 min, 10 min later into the reaction mixture was added respectively either 1.3 g (0.01 mol) tetronic acid (**I**) or 1.43 g (0.01 mol) of 2-naphthylamine (**III**), and the boiling was continued for 20–40 min. On cooling the separated precipitate was filtered off, washed with ether, and recrystallized from a mixture ethanol–benzene, 1:1.

c. A solution of 0.01 mol of an appropriate 3-aryl-methylene-2,4(3*H*,5*H*)-furan-2,4-dione **Va–Vk** and 0.01 mol 2-naphthylamine (**III**) in 20 ml of ethanol was boiled till the beginning of crystals precipitation. On cooling the separated precipitate was filtered off, washed with ether, and recrystallized from a mixture ethanol–benzene, 1:1.

8,11-Dihydro-11-phenylbenzo[f]furo[3,4-*b*]-quinolin-10(7H)-one (VIa). Yield 72%, colorless crystals, mp 270°C. IR spectrum, cm^{-1} : 3220, 3190, 1718, 1642, 1590, 1541, 1470, 1442, 1361, 1235, 1100, 813. ¹H NMR spectrum, δ , ppm: 4.90 d.d (2H, CH₂OCO), 5.43 s (1H, CH), 6.80–7.10, 7.20–7.43, 7.60–7.90 m (11H_{arom}), 10.12 s (1H, NH). Found, %: C 80.53; H 4.80; N 4.43. C₂₁H₁₅NO₂. Calculated, %: C 80.51; H 4.79; N 4.47.

8,11-Dihydro-11-(4-chlorophenyl)benzo[f]furo[3,4-*b*]-quinolin-10(7H)-one (VIb). Yield 82%, colorless

crystals, mp 295°C. IR spectrum, cm^{-1} : 3229, 1726, 1645, 1541, 1520, 1468, 1321, 1223, 1080, 854, 813. ^1H NMR spectrum, δ , ppm: 4.93 d.d (2H, CH_2OCO), 5.69 s (1H, CH), 7.00–7.20, 7.26–7.57, 7.67–8.10 m (10H_{arom}), 10.31 s (1H, NH). Found, %: C 72.60; H 4.02; Cl 10.10; N 4.04. $\text{C}_{21}\text{H}_{14}\text{ClNO}_2$. Calculated, %: C 72.62; H 4.03; Cl 10.08; N 4.03.

8,11-Dihydro-11-(4-bromophenyl)benzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-one (VIc). Yield 84%, colorless crystals, mp 340°C. IR spectrum, cm^{-1} : 3230, 1720, 1647, 1531, 1513, 1484, 1213, 1011, 743, 562. ^1H NMR spectrum, δ , ppm: 4.95 d.d (2H, CH_2OCO), 5.64 s (1H, CH), 7.00–7.20, 7.26–7.57, 7.67–8.10 m (10H_{arom}), 10.31 s (1H, NH). Found, %: C 64.29; H 3.60; Br 20.38; N 3.60. $\text{C}_{21}\text{H}_{14}\text{BrNO}_2$. Calculated, %: C 64.28; H 3.57; Br 20.41; N 3.57.

8,11-Dihydro-11-(4-hydroxyphenyl)benzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-one (VIId). Yield 47%, colorless crystals, mp 268–269°C. IR spectrum, cm^{-1} : 3330, 3307, 1750, 1731, 1640, 1536, 1479, 1324, 1217, 1008, 560. ^1H NMR spectrum, δ , ppm: 4.80 d.d (2H, CH_2OCO), 5.52 s (1H, CH), 6.12–6.56 m (2H_{arom}), 6.90–7.05 m (2H_{arom}), 7.18–7.40 m (3H_{arom}), 7.62–7.85 m (3H_{arom}), 8.64 (1H, OH), 10.00 s (1H, NH). Found, %: C 76.60; H 4.56; N 4.21. $\text{C}_{21}\text{H}_{15}\text{NO}_3$. Calculated, %: C 76.59; H 4.56; N 4.25.

8,11-Dihydro-11-(4-methoxyphenyl)benzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-one (VIe). Yield 47%, colorless crystals, mp 278°C. IR spectrum, cm^{-1} : 3326, 3310, 2850, 2744, 1743, 1667, 1532, 1515, 1482, 1319, 1225, 973, 552. ^1H NMR spectrum, δ , ppm: 3.18 s (3H, OMe), 4.72 d.d (2H, CH_2OCO), 5.49 s (1H, CH), 6.10–6.48 m (2H_{arom}), 6.90–7.08 m (2H_{arom}), 7.22–7.34 m (3H_{arom}), 7.60–7.73 m (3H_{arom}), 10.08 s (1H, NH). Found, %: C 77.00; H 4.95; N 4.10. $\text{C}_{22}\text{H}_{17}\text{NO}_3$. Calculated, %: C 76.96; H 4.95; N 4.08.

8,11-Dihydro-11-(4-dimethylaminophenyl)benzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-one (VI f). Yield 58%, colorless crystals, mp 224°C. IR spectrum, cm^{-1} : 3321, 3307, 2236, 2054, 1715, 1703, 1662, 1513, 1484, 1387, 1312, 1222, 964, 542. ^1H NMR spectrum, δ , ppm: 2.75 s (6H, 2Me), 4.80 d.d (2H, CH_2OCO), 5.50 s (1H, CH), 6.40–6.60 m, 7.00–7.40, 7.60–7.80 m (10H_{arom}), 9.95 s (1H, NH). Found, %: C 77.54; H 5.60; N 7.88. $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_2$. Calculated, %: C 77.52; H 5.62; N 7.86.

8,11-Dihydro-11-(4-diethylaminophenyl)benzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-one (VIg). Yield 54%, colorless crystals, mp 300°C. IR spectrum, cm^{-1} : 3329,

3294, 2185, 2010, 1727, 1711, 1689, 1532, 1472, 1376, 1334, 1235, 992, 573. ^1H NMR spectrum, δ , ppm: 1.09 t (6H, $2\text{CH}_2\text{Me}$), 3.25 q (4H, $2\text{CH}_2\text{Me}$), 4.78 d.d (2H, CH_2OCO), 5.47 s (1H, CH), 6.35–6.52 m (2H_{arom}), 6.88–7.09 m (2H_{arom}), 7.18–7.35 m (3H_{arom}), 7.61–7.77 m (3H_{arom}), 9.89 s (1H, NH). Found, %: C 78.11; H 6.24; N 7.31. $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}_2$. Calculated, %: C 78.12; H 6.25; N 7.29.

8,11-Dihydro-11-(3,4-dimethoxyphenyl)benzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-one (VIh). Yield 50%, colorless crystals, mp 238°C. IR spectrum, cm^{-1} : 3310, 3230, 2843, 2213, 2126, 2051, 1722, 1693, 1660, 1524, 1471, 1368, 1325, 1211, 967, 564. ^1H NMR spectrum, δ , ppm: 3.65 (6H, 2OMe), 4.92 d.d (2H, CH_2OCO), 5.61 s (1H, CH), 6.42–6.68 m (2H_{arom}), 7.00 s (1H_{arom}), 7.20–7.36 m (3H_{arom}), 7.62–7.81 m (3H_{arom}), 9.95 s (1H, NH). Found, %: C 73.80; H 5.36; N 3.72. $\text{C}_{23}\text{H}_{20}\text{NO}_4$. Calculated, %: C 73.79; H 5.34; N 3.74.

8,11-Dihydro-11-(4-hydroxy-3-methoxyphenyl)benzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-one (VIi). Yield 82%, colorless crystals, mp 298–300°C. IR spectrum, cm^{-1} : 3338, 3315, 3268, 2846, 2739, 1745, 1662, 1643, 1529, 1513, 1472, 1325, 1218, 1009, 565. ^1H NMR spectrum, δ , ppm: 3.20 s (3H, OMe), 4.90 d.d (2H, CH_2OCO), 5.58 s (1H, CH), 6.39 d (1H_{arom}), 6.57 d (1H_{arom}), 6.95 s (1H_{arom}), 7.25–7.40 m (3H_{arom}), 7.85 m (3H_{arom}), 8.68 s (1H, OH), 10.20 s (1H, NH). Found, %: C 73.34; H 4.98; N 3.87. $\text{C}_{22}\text{H}_{18}\text{NO}_4$. Calculated, %: C 73.33; H 5.00; N 3.89.

8,11-Dihydro-11-(4-hydroxy-3-ethoxyphenyl)benzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-one (VIj). Yield 78%, colorless crystals, mp 268–270°C. IR spectrum, cm^{-1} : 3324, 3318, 3262, 2831, 2745, 1739, 1658, 1642, 1534, 1513, 1471, 1319, 1216, 1010, 562. ^1H NMR spectrum, δ , ppm: 1.28 t (3H, OCH_2Me), 3.90 m (2H, OCH_2Me), 4.90 d.d (2H, CH_2OCO), 5.57 s (1H, CH), 6.39 d (1H_{arom}), 6.53 d (1H_{arom}), 6.92 s (1H_{arom}), 7.25–7.38 m (3H_{arom}), 7.87 m (3H_{arom}), 8.59 s (1H, OH), 10.19 s (1H, NH). Found, %: C 73.80; H 5.35; N 3.73. $\text{C}_{23}\text{H}_{20}\text{NO}_4$. Calculated, %: C 73.79; H 5.34; N 3.74.

8,11-Dihydro-11-(3,4-methylenedioxyphenyl)benzo[*f*]furo[3,4-*b*]quinolin-10(7*H*)-one (VIk). Yield 84%, colorless crystals, mp 330°C. IR spectrum, cm^{-1} : 3278, 3250, 1724, 1650, 1618, 1598, 1526, 1485, 1467, 1431, 1353, 1248, 1211, 1028, 1012, 813. ^1H NMR spectrum, δ , ppm: 4.80 d.d (2H, CH_2OCO), 5.60 s (1H, CH), 5.87 d (2H, OCH_2O), 6.60–6.65 m (3H_{arom}), 7.20–

7.38 m (3H_{arom}), 7.70–7.80 m (3H_{arom}), 9.98 s (1H, NH). Found, %: C 73.96; H 4.22, N 3.90. C₂₂H₁₅NO₄. Calculated, %: C 73.95; H 4.20; N 3.92.

11-(1,3-Benzodioxol-5-yl)benzo[*f*]furo[3,4-*b*]-quinolin-10(8*H*)-one (VIIIk). To a solution of 1.1 g (3 mmol) of compound **VIk** in 5 ml of acetic acid and 2 ml of hydrochloric acid was added 0.28 (4 mmol) of sodium nitrite, and the mixture was stirred at room temperature for 40 min. The reaction mixture was neutralized with a saturated solution of sodium hydrogen carbonate, the separated precipitate was filtered off and recrystallized from DMF. Yield 0.93 g (86%), colorless crystals, mp 295°C. IR spectrum, cm⁻¹: 1740, 1214, 1012. ¹H NMR spectrum, δ, ppm: 5.47 s (2H, C⁸H), 6.18 s (2H, OCH₂O), 6.70–8.40 m (9H_{apOm}). Found, %: C 74.39; H 3.66; N 3.93. C₂₂H₁₃NO₄. Calculated, %: C 74.36; H 3.69; N 3.94.

1-(1,3-Benzodioxol-5-yl)-3-(hydroxymethyl)-benzo[*f*]quinoline-2-carbohydrazide (VIIIk). A mixture of 0.36 g (1 mmol) of compound **VIk** and 1 ml of hydrazine hydrate in 15 ml of ethanol was boiled for 1 h. On cooling the separated precipitate was filtered off, washed with ethanol (3 × 5 ml), and recrystallized from DMF. Yield 0.37 g (95%), colorless crystals, mp 220°C (decomp.). IR spectrum, cm⁻¹: 3337, 3192, 1626, 1479, 1231, 1036. ¹H NMR spectrum, δ, ppm: 4.22 s (2H, CH₂OH), 4.60–4.82 m (2H, NHNH₂), 4.95–5.30 m (1H, NHNH₂), 6.14 s (2H, OCH₂O), 6.65–8.25 m (9H_{arom}), 9.27 s (1H, OH). Found, %: C 68.19; H 4.45; N 10.89. C₂₂H₁₇N₃O₄. Calculated, %: C 68.21; H 4.42; N 10.85.

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