

Perhydrofuro[3,2-*c*]-, Perhydropyrano[3,2-*c*]-, and 4-Ethoxy-2-(5-R-furan-2-yl)tetrahydroquinolines. Synthesis and Transformations

F. I. Zubkov, V. P. Zaitsev, A. M. Piskareva, M. N. Eliseeva, E. V. Nikitina,
N. M. Mikhailova, and A. V. Varlamov

Russian University of Peoples' Friendship, ul. Miklukho-Maklaya 6, Moscow, 117198 Russia
e-mail: fzubkov@sci.pfu.edu.ru

Received July 20, 2009

Abstract—Partly hydrogenated 2-[5-methyl(bromo, nitro)furan-2-yl]-substituted furo[3,2-*c*]quinolines, pyrano[3,2-*c*]quinolines, and 4-ethoxyquinolines were synthesized by the imino Diels–Alder (Povarov) reaction. Cycloadditions of these compounds with maleic, citraconic, and dibromomaleic anhydrides, as well as with acryloyl, methacryloyl, and cinnamoyl chlorides led to the formation of substituted epoxyisoindolo[2,1-*a*]quinolines and -quinolinecarboxylic acids. Oxidation of the double C=C bond in the adducts, esterification of the carboxy group, and aromatization of the 7-oxabicycloheptene fragment were accomplished.

DOI: 10.1134/S1070428010080142

We previously synthesized 4-substituted 6-R-2-furyltetrahydroquinolines and those fused at the C³–C⁴ bond and studied their [4+2]-cycloaddition reactions with maleic anhydride and acryloyl chloride [1–3] and the effect of electronic properties of the R substituents in the aryl fragment on the cyclization of *N*-furfurylideneanilines with vinyl ethers and vinyl amides to the corresponding tetrahydroquinolines (Povarov reaction) [4, 5].

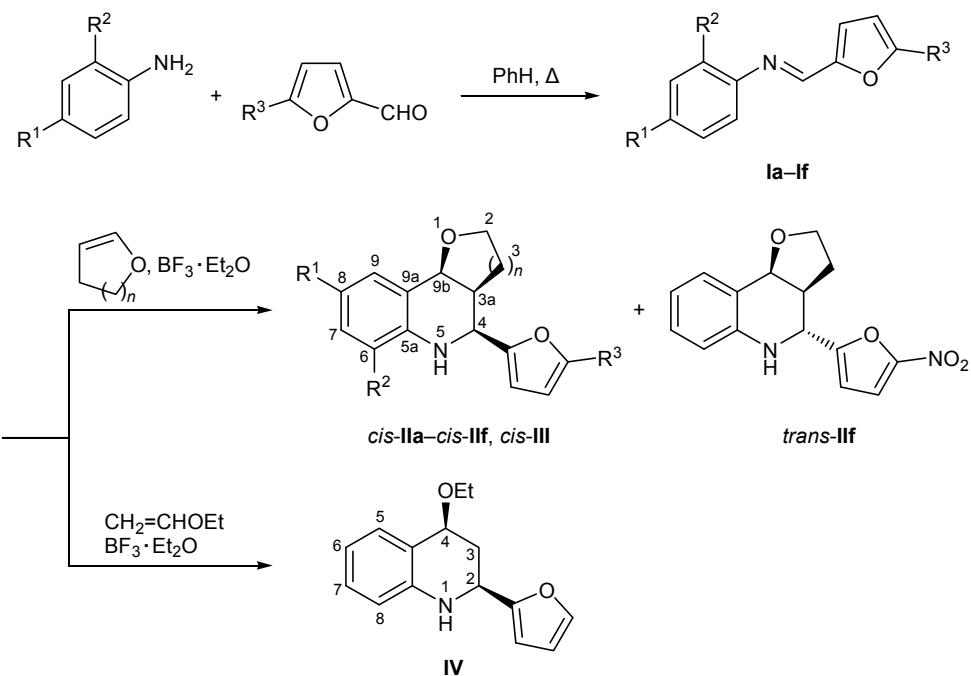
The goal of the present work was to study the behavior of *N*-furfurylideneanilines with different substituents in position 5 of the furan ring in the Povarov reaction and reveal general relations holding in the cycloaddition of 2-furyltetrahydroquinolines thus obtained with maleic, citraconic, and dibromomaleic anhydrides, as well as with substituted acryloyl chlorides. *N*-Furfurylideneanilines **I** were synthesized by condensation of the corresponding 5-substituted furan-2-carbaldehydes with *ortho*- and *para*-substituted anilines. Compounds **I** were brought into cycloadditions with dihydrofuran, dihydropyran, and ethyl vinyl ether (Scheme 1). The reactions were carried out in diethyl ether or benzene at 0–20°C in the presence of boron trifluoride–diethyl ether complex (5 mol %).

We previously showed that electron-withdrawing substituents in the aniline fragment reduce the yield of

furyl-substituted tetrahydroquinolines [1]. In the present work we found that increase in the electron-acceptor power of the substituent R³ in the furan ring favors formation of cycloaddition products **II**. Schiff base **Ic** having a hydroxy group in the *ortho*-position of the benzene ring was considerably less active in the Povarov reaction. According to the ¹H NMR data, 5-nitrofuryl-substituted tetrahydroquinoline **IIf** was formed as an equimolar mixture of two stereoisomers differing by mutual arrangement of the 5-nitrofuryl substituent and fused tetrahydrofuran ring. The coupling constants for the *cis* isomer of **IIf** are J_{4,3a} = 2.7, J_{3a,9b} = 7.4 Hz, and for the *trans* isomer, J_{4,3a} = 5.4, J_{3a,9b} = 10.1 Hz. Tetrahydroquinolines **III** and **IV** were reported by us previously [1, 2].

2-Furyl-substituted tetrahydroquinolines **IIa**, **IIc**–**IIe**, **III**, and **IV** readily reacted with maleic anhydride at 0–5°C, following the Diels–Alder pattern (Scheme 2), to produce mixtures of stereoisomeric *exo*-tetrahydrofurano- (**Va**, **Vc**–**Ve**), tetrahydropyrano- (**VI**), and 4-ethoxyisoindolo[2,1-*a*]quinolinecarboxylic acids (**VII**). In the reactions with furano- and pyranoquinolines **IIa**, **IId**, **IIe**, and **III**, the major products were isomers **V** and **VI** with *trans* orientation of the epoxy bridge and the fused heteroring, whereas 8-hydroxy-substituted derivative **IIe** gave rise to only *trans* isomer **Vc**. The adduct obtained from 4-ethoxyquinoline

Scheme 1.



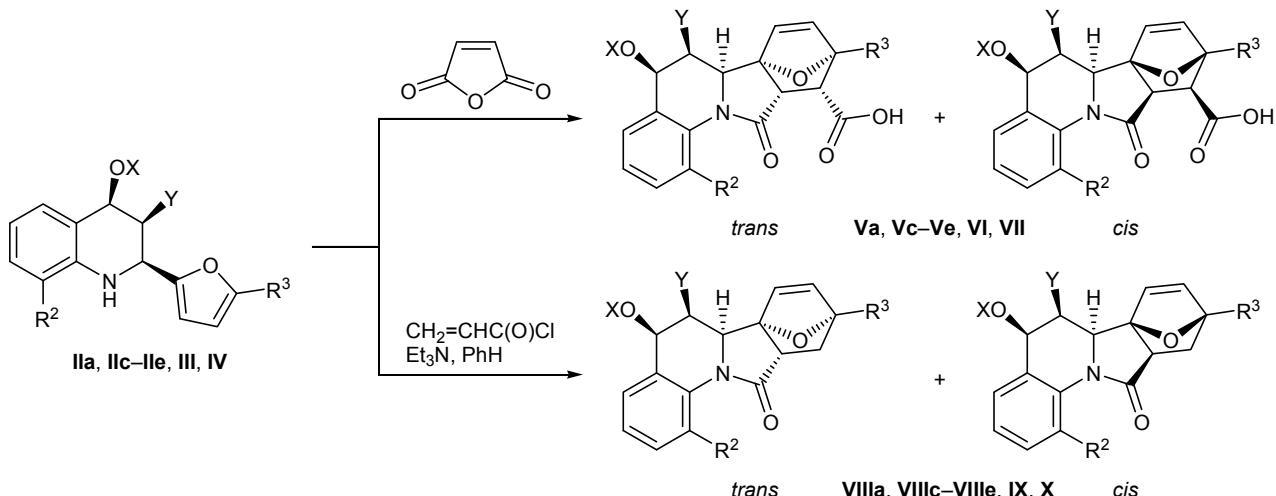
I, II, R² = R³ = H, R¹ = H (**a**), Ac (**b**); R¹ = R³ = H, R² = HO (**c**); R¹ = R² = H, R³ = Me (**d**), Br (**e**), O₂N (**f**); **III**, R¹ = R² = R³ = H; **II**, n = 1; **III**, n = 2.

IV was represented mainly by *cis* isomer **VII**. The cycloaddition of maleic anhydride at 110°C was stereospecific due to reversibility of the Diels–Alder reaction. The reactions with fused quinolines **IIa**, **IId**, **IIe**, and **III** afforded only *trans* isomers **Va**, **Vd**, **Ve**, and **VI**, while *cis* isomer **VII** was formed from 4-ethoxytetrahydroquinoline **IV**. Analogous results were obtained when mixtures of isomeric adducts **V**–**VII** were heated at 110°C. The least basic acetyl-

substituted tetrahydroquinoline **IIb** was almost inert in cycloaddition reactions.

The cycloaddition of acryloyl chloride to fused quinolines **IIa**, **IIc**–**IIe**, and **III** in boiling benzene in the presence of triethylamine was not stereoselective, and mixtures of *cis*- and *trans*-isomeric epoxyisoindolo[2,1-*a*]tetrahydroquinolines **VIIIa**, **VIIIc**–**VIIIe**, and **IX** were formed (Scheme 2). However, 4-ethoxytetrahydroquinoline **IV** reacted with acryloyl chloride

Scheme 2.



II, V, VIII, XY = (CH₂)₂; **III, VI, IX, XY** = (CH₂)₃; **IV, VII, X, X** = Et, Y = H.

Diels–Alder reactions of furyl-substituted quinolines **IIa**, **IIc–IIe**, **III**, and **IV** with maleic anhydride and acryloyl chloride at different temperatures

Quinoline no.	R ²	R ³	X	Y	Adduct with maleic anhydride			Adduct with acryloyl chloride, 80°C	
					comp. no.	0–5°C, <i>trans/cis</i> ratio (yield, %)	110°C, isomer (yield, %)	comp. no.	<i>trans/cis</i> ratio (yield, %)
IIa	H	H	(CH ₂) ₂		Va [1]	71/29 (65)	<i>trans</i> (85)	VIIIa [1]	45/55 (90)
IIc	OH	H	(CH ₂) ₂		Vc	<i>trans</i> (94)	— ^a	VIIIc	50/50 (87)
IId	H	Me	(CH ₂) ₂		Vd	50/50 (79)	<i>trans</i> (62)	VIIId	50/50 (87)
IIe	H	Br	(CH ₂) ₂		Ve	65/35 (95)	<i>trans</i> (75)	VIIIe	50/50 (44)
III	H	H	(CH ₂) ₃		VI [1]	75/25 (58)	<i>trans</i> (66)	IX [1]	33/66 (80)
IV	H	H	Et	H	VII [1]	25/75 (88)	<i>cis</i> (99)	X [1]	<i>cis</i> (53)

^a No experiment was performed.

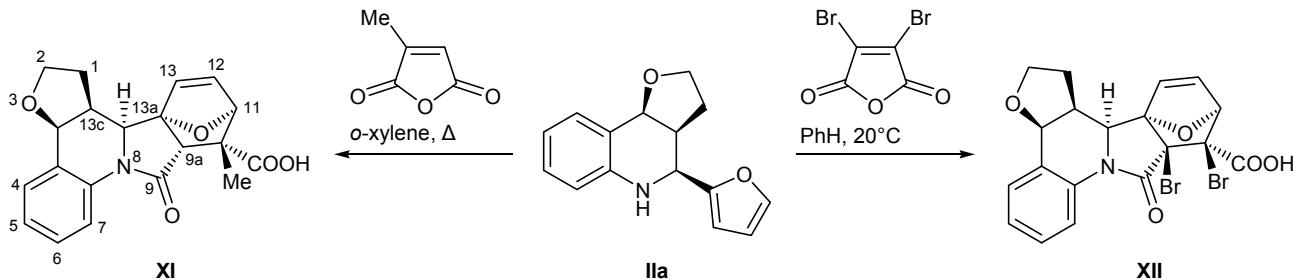
strictly stereoselectivity, yielding only *exo-cis*-adduct **X**. The composition of mixtures of *trans* and *cis* isomers **VIIIa**, **VIIIc–VIIIe**, and **IX** remained unchanged on heating in xylene. The presence of a methyl group or bromine atom on C⁵ in the furan ring of compounds **IId** and **IIe** almost did not affect the stereoselectivity in the cycloadditions with maleic anhydride and acryloyl chloride (see table).

The steric structure of isomeric adducts **V–VII** was determined taking into account our previous data [1] on the chemical shifts of aromatic protons in the *ortho* position with respect to the nitrogen atom (7-H or 8-H in furano- and pyranoquinolines **Va**, **Vd**, **Ve**, and **VI** and 1-H in 4-ethoxy derivative **VII**). In the ¹H NMR spectra of these adducts, signals from the above protons in the *trans* isomers are located in a stronger field (by 0.6–0.8 ppm) relative to the corresponding signals of the *cis* isomers. The *ortho* position with respect to the nitrogen atom in *trans*-adduct **Vc** is occupied by hydroxy group; therefore, its structure was determined by comparing the chemical shifts of 3a-H and 13b-H with those of analogous protons in isomers **Va**. Stereosomeric adducts **VIIIa**, **VIIIc–VIIIe**, **IX**, and **X** were assigned to the *cis* or *trans* series by analogy with compounds **Va**, **Vc–Ve**, **VI**, and **VII**.

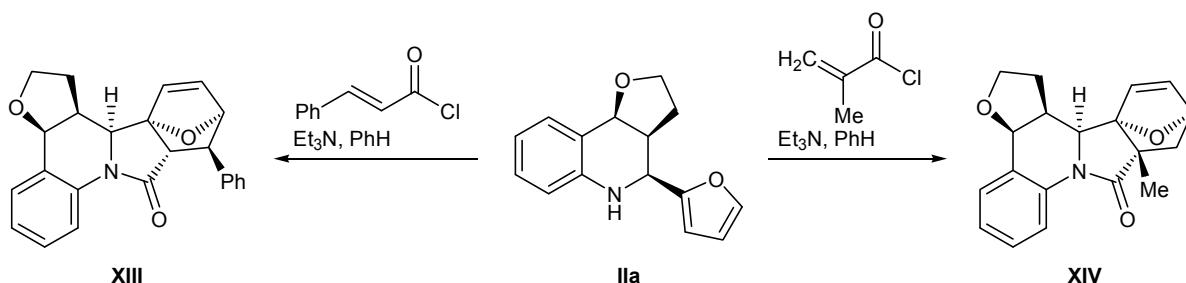
Citraconic anhydride turned out to be less reactive than maleic anhydride in the cycloaddition to compound **IIa**. The corresponding *exo,trans*-adduct **XI** was obtained only by prolonged heating of the reactants in boiling xylene using a large excess of citraconic anhydride. The methyl and carboxy groups in the adduct are attached to the same carbon atom (Scheme 3). The structure of compound **XI** was determined by measuring nuclear Overhauser effects (NOE) in the ¹H NMR spectra. The NOE values $\eta_{11\text{-H}}\{10\text{-Me}\} = 4.6$, $\eta_{12\text{-H}}\{10\text{-Me}\} = 5.5$, and $\eta_{9\text{a-H}}\{10\text{-Me}\} = 7.0$ indicated *endo* orientation of the methyl group relative to the bridging oxygen atom in the oxabicycloheptene fragment and *cis* orientation of 9a-H and 10-Me. The absence of NOE between 9a-H and 13b-H is consistent with their *trans* orientation with respect to each other. Relatively large NOEs for the 1-H_A, 13b-H, 13c-H, and 3a-H protons ($\eta_{13\text{c-H}}\{1\text{-H}_A\} = 4.0$, $\eta_{13\text{b-H}}\{13\text{c-H}\} = 5.2$, $\eta_{3\text{a-H}}\{13\text{c-H}\} = 6.5$) allowed us to assign *cis* orientation to 1-H_A and 13c-H, as well as to 3a-H, 13c-H, and 13b-H.

Dibromomaleic anhydride reacted with furoquinoline **IIa** even at 20°C to form *exo,trans*-adduct **XII**. The Diels–Alder reactions of compound **IIa** with methacryloyl and cinnamoyl chlorides occurred in

Scheme 3.



Scheme 4.



a way similar to the reaction with acetyl chloride. In both cases, the cycloaddition was stereoselective, and the corresponding *exo,trans*-adducts **XIII** and **XIV** were isolated in good yields (Scheme 4). By esterification of *trans*-isomeric epoxyfuranoisoindoloquinolinecarboxylic acids **Va** and **Vd** with methanol we obtained mixtures of *trans* and *cis* isomers of esters **XVa** and **XVd** in overall yields of 61 and 80%, respectively. Presumably, the reason is retro-Diels–Alder reaction of the initially formed *trans*-esters (Scheme 5) [1]. According to the ¹H NMR data, the *trans/cis* isomer ratios were ~7:1 for compound **XVa** and 2:1 for ester **XVb**. No retro-Diels–Alder reaction of *trans*-esters **XVI** and **XVII** was observed in the esterification of *trans*-isomeric carboxylic acids **VI** and **XI**.

Likewise, retro-Diels–Alder reaction did not accompany esterification of *cis*-acid **VII**, and the corresponding *cis*-ester **XVIII** was obtained in 78% yield. The major *trans* isomers of esters **XVa** and **XVd** were isolated as individual substances by fractional crystallization.

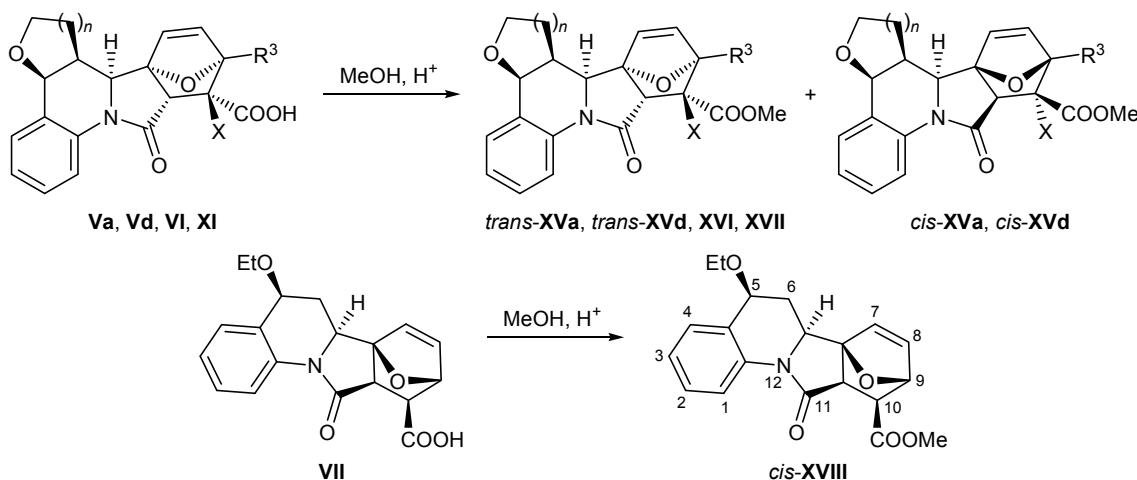
The double bond in the oxabicycloheptene fragment of *trans*-isomeric esters **XVa**, **XVd**, **XVI**, **XVII**,

cis-ester **XVIII**, *cis* isomer **X**, and *trans* isomers **XIII** and **XIV** was oxidized with *m*-chloroperoxybenzoic acid in methylene chloride (Scheme 6). The oxidation products were the corresponding *cis*-diepoxy derivatives **XIX–XXII** which attract interest as substrates for further transformations [6].

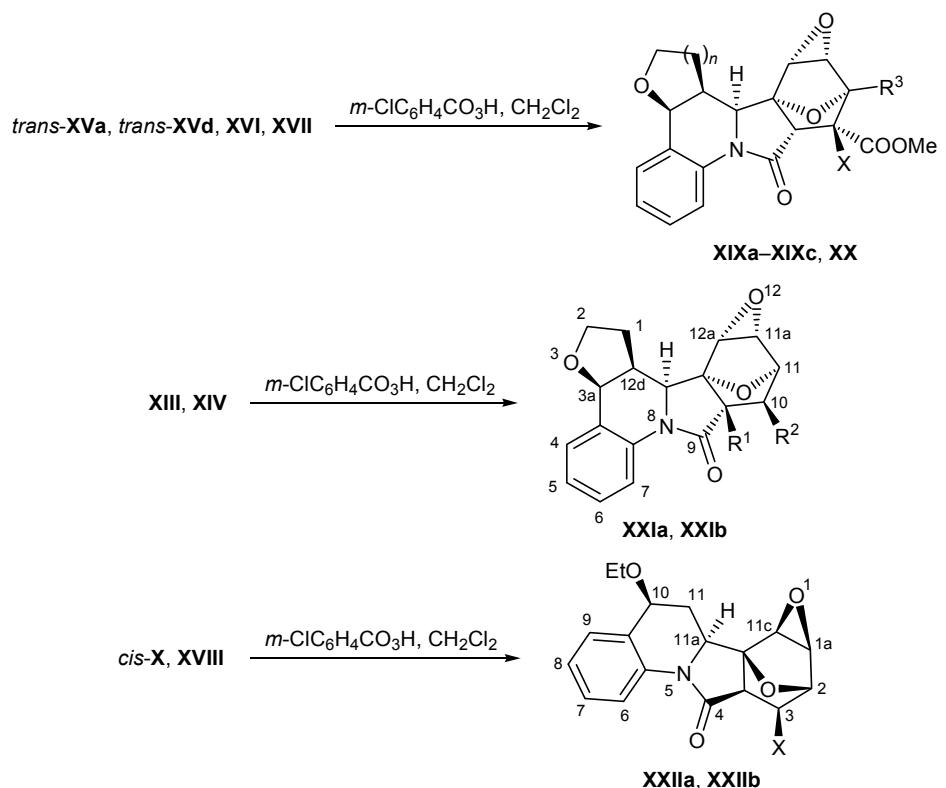
The *exo* configuration of the oxirane ring fused to the 7-oxabicycloheptane fragment and correspondingly *cis* orientation of the oxygen bridges with respect to each other unambiguously followed from the coupling constants of the 11a-H, 11-H, and 12a-H protons in furan-fused compounds **XIX** and **XXI** and of 12a-H, 12-H, and 13a-H in pyran-fused analog **XX**: $J_{11a,12a} = J_{12a,13a} = 3.3$, $J_{11,11a} = J_{12,12a} = 0$ Hz; the corresponding coupling constants in ethoxy-substituted diepoxides **XXII** were $J_{1a,11c} = 3.2$ – 3.4 , $J_{1a,2} = 0$ Hz. The absence of appreciable vicinal couplings (3J) for the protons in the bridgehead positions of the oxabicyclic fragment in **XIX–XXII** unambiguously indicates *exo* orientation of all substituents [7, 8].

Treatment of compounds **Va**, **VI**, and **VIIIa** with orthophosphoric acid at 85°C resulted in cleavage of the epoxy bridge in the oxabicycloheptene fragment

Scheme 5.



Scheme 6.



XIX, $n = 1$; **XX**, $n = 2$; **XIX**, $R^3 = H$, $X = H$ (**a**), Me (**c**); $R^3 = Me$, $X = H$ (**b**); **XX**, $R^3 = X = H$; **XXI**, $R^1 = H$, $R^2 = Ph$ (**a**); $R^1 = Me$, $R^2 = H$ (**b**); **XXII**, $X = H$ (**a**), CO_2Me (**b**).

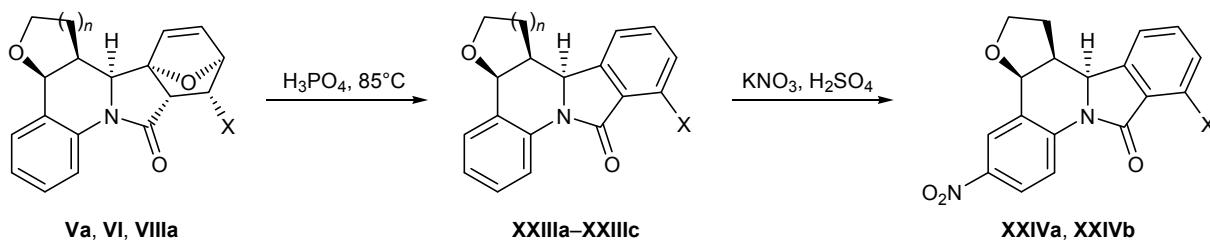
and subsequent aromatization with formation of compounds **XXIIIa–XXIIIc** in 35–89% yield (Scheme 7) [9]. Isoindolo[2,1-*a*]quinolines **XXIIIa** and **XXIIIb** were subjected to nitration with a mixture of potassium nitrate and sulfuric acid. The reaction was regioselective, and the corresponding 5-nitro derivatives **XXIVa** and **XXIVb** were formed in moderate yields [10].

EXPERIMENTAL

Commercial reagents from Acros Organics were used without additional purification. The IR spectra were recorded on an Infralyum FT-801 spectrometer

with Fourier transform from samples prepared as KBr pellets. The ^1H NMR spectra were measured on a Bruker WH-400 spectrometer (400 MHz) at 30°C using the residual solvent signal as reference (CHCl_3 , δ 7.26 ppm; $\text{DMSO}-d_5$, δ 2.49 ppm). The ^{13}C NMR spectra were obtained on a Bruker Avance 600 instrument at 150 MHz; the chemical shifts were measured relative to the central peak of the $\text{DMSO}-d_6$ multiplet (δ_{C} 39.96 ppm). Signals in the NMR spectra were assigned using two-dimensional HMQC and COSY-45 correlation techniques; NOE experiments were performed according to one-dimensional procedure without preliminary degassing of samples. The mass spec-

Scheme 7.



XXIII, $n = 1$ (**a**, **b**), 2 (**c**); $X = CO_2H$ (**a**, **c**), H (**b**).

tra (electron impact, 70 eV) were recorded on a Thermo Focus DSQ II GC-MS system (ion source temperature 200°C, Varian FactorFour VF-5ms chromatographic column) or on a Thermo Trace DSQ mass spectrometer (ion source temperature 200°C, direct sample admission into the ion source). Thin-layer chromatography was performed on Sorbfil plates (spots were visualized by treatment with iodine vapor). Neutral aluminum oxide (Fluka 507S, grain size 0.05–0.15 mm) was used for column chromatography.

Cycloaddition of Schiff bases Ia–If to dihydrofuran (general procedure). A solution of 0.2 mol of Schiff base I in 100 ml of anhydrous benzene (**Id**) or methylene chloride (**Ib**, **Ic**, **Ie**, **If**) was cooled to 0°C, 0.63 ml (5 mmol) of boron trifluoride-diethyl ether complex was added under stirring, and 16.6 ml (0.22 mol) of dihydrofuran was added dropwise under stirring. The mixture was stirred for 2 h at 0–5°C and for 3 h at 20°C, 3–4 ml of 25% aqueous ammonia was added until alkaline reaction, and the mixture was concentrated under reduced pressure. The residue was a dark viscous oily material which was purified by column chromatography using ethyl acetate–hexane (1:10) as eluent.

1-[*(3aS*,4S*,9bS*)-4-(2-Furyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinolin-8-yl]ethanone (IIb).* Yield 37%. Colorless crystals, mp 179–181°C (from hexane–ethyl acetate), R_f 0.26 (hexane–ethyl acetate, 2:1). IR spectrum, ν , cm⁻¹: 3288 (NH), 1659 (C=O). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.89 m (1H, 3-H), 2.14 d.q (1H, 3-H, ³J = 8.6, ²J = 12.5 Hz), 2.52 s (3H, COMe), 2.97 d.d.q (1H, 3a-H, $J_{3a,4}$ = 3.2, $J_{3a,9b}$ = 7.6, $J_{3a,3}$ = 8.2 Hz), 3.74 d.t (1H, 2-H, ²J = ³J = 8.6 Hz), 3.82 q (1H, 2-H, ²J = 8.4, ³J = 4.4 Hz), 4.44 br.s (NH), 4.81 d (1H, 4-H, $J_{3a,4}$ = 3.2 Hz), 5.22 d (1H, 9b-H, $J_{3a,9b}$ = 7.6 Hz), 6.30 d.d (1H, 3'-H, ⁴J = 0.8, ³J = 3.2 Hz), 6.38 d.d (1H, 4'-H, $J_{5',4'}$ = 1.8, $J_{4',3'}$ = 3.2 Hz), 6.59 d (1H, 6-H, $J_{6,7}$ = 8.5 Hz), 7.40 d.d (1H, 5'-H, $J_{5',4'}$ = 1.8, $J_{5',3'}$ = 0.8 Hz), 7.74 d.d (1H, 7-H, $J_{7,9}$ = 2.0, $J_{6,7}$ = 8.5 Hz), 7.97 d (1H, 9-H, $J_{7,9}$ = 2.0 Hz). Mass spectrum, m/z (I_{rel} , %): 283 (100) [M]⁺, 268 (22), 254 (13), 238 (90), 210 (9), 198 (6), 172 (15), 167 (5), 103 (5), 81 (6), 43 (7). Found, %: C 72.31; H 6.21; N 4.78. C₁₇H₁₇NO₃. Calculated, %: C 72.07; H 6.05; N 4.94. M 283.12.

(3aS*,4S*,9bS*)-4-(2-Furyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinolin-6-ol (IIc). Yield 14%. Colorless crystals, mp 144–145°C (from hexane–ethyl acetate), R_f 0.73 (hexane–ethyl acetate, 6:1). IR spectrum, ν , cm⁻¹: 3386, 3216 (NH, OH). ¹H NMR spec-

trum (CDCl₃), δ , ppm: 1.85 m (1H, 3-H), 2.24 d.q (1H, 3-H, $J_{2,3}$ = $J_{3a,3}$ = 8.8, ²J = 12.3 Hz), 2.99 d.q (1H, 3a-H, $J_{3a,4}$ = 3.0, $J_{3a,9b}$ = 7.9, $J_{3a,3}$ = 8.7, $J_{3a,3}$ = 8.8 Hz), 3.82–3.74 m (2H, 2-H), 4.69 d (1H, 4-H, $J_{3a,4}$ = 3.0 Hz), 5.28 d (1H, 9b-H, $J_{3a,9b}$ = 7.9 Hz), 5.54 br.s (OH, NH), 6.34 d.d (1H, 3'-H, $J_{5',3'}$ = 0.7, $J_{4',3'}$ = 3.2 Hz), 6.38 d.d (1H, 4'-H, $J_{5',4'}$ = 1.7, $J_{4',3'}$ = 3.2 Hz), 6.62 d.d (1H, 7-H, $J_{7,9}$ = 0.7, $J_{7,8}$ = 7.6 Hz), 6.68 d.t (1H, 8-H, $J_{7,8}$ = $J_{8,9}$ = 7.6 Hz), 6.97 d.d (1H, 9-H, $J_{7,9}$ = 0.7, $J_{8,9}$ = 7.6 Hz), 7.40 d.d (1H, 5'-H, $J_{5',4'}$ = 1.7, $J_{5',3'}$ = 0.7 Hz). Mass spectrum, m/z (I_{rel} , %): 257 (100) [M]⁺, 212 (61), 184 (11), 146 (30), 121 (48), 103 (42), 93 (36), 77 (55), 65 (23), 55 (31), 39 (47). Found, %: C 70.45; H 5.58; N 5.25. C₁₅H₁₅NO₃. Calculated, %: C 70.02; H 5.88; N 5.44. M 257.11.

(3aS*,4S*,9bS*)-4-(5-Methylfuran-2-yl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (IId). Yield 40%. Colorless crystals, mp 79–81°C (from hexane–ethyl acetate), R_f 0.61 (hexane–ethyl acetate, 8:1). IR spectrum: ν 3303 cm⁻¹ (NH). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.87 m (1H, 3-H), 2.22 d.d (1H, 3-H, $J_{3a,3}$ = 9.1 Hz), 2.30 d (3H, Me), 2.95 d.d.q (1H, 3a-H, $J_{3a,4}$ = 2.7, $J_{3a,9b}$ = 9.4, $J_{3a,3}$ = 9.1 Hz), 3.76 d.t (1H, 2-H, ²J = 8.3 Hz), 3.80 q (1H, 2-H, ²J = 8.3 Hz), 3.93 br.s (NH), 4.64 d (1H, 4-H, $J_{3a,4}$ = 2.7 Hz), 5.23 d (1H, 8b-H, $J_{3a,9b}$ = 9.4 Hz), 5.94 d.q (1H, 4'-H, $J_{4',3'}$ = 3.0 Hz), 6.15 br.d (1H, 3'-H, $J_{4',3'}$ = 3.0 Hz), 6.59 d.d (1H, 9-H, $J_{7,9}$ = 1.0, $J_{8,9}$ = 7.9 Hz), 6.81 d.t (1H, 7-H, $J_{7,9}$ = 1.0, $J_{7,8}$ = $J_{6,7}$ = 7.6 Hz), 7.08 d.t (1H, 8-H, $J_{7,8}$ = $J_{8,9}$ = 7.7, $J_{6,8}$ = 1.5 Hz), 7.34 br.d (1H, 6-H, $J_{6,7}$ = 7.5 Hz). Mass spectrum, m/z (I_{rel} , %): 255 (34) [M]⁺, 210 (59), 167 (13), 144 (17), 130 (44), 117 (27), 95 (43), 77 (40), 65 (22), 51 (32), 43 (100), 39 (41). Found, %: C 75.09; H 6.45; N 5.85. C₁₆H₁₇NO₂. Calculated, %: C 75.27; H 6.71; N 5.49. M 255.13.

(3aS*,4S*,9bS*)-4-(5-Bromofuran-2-yl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline (IIe). Yield 54%. Colorless crystals, mp 74–75°C (from hexane–ethyl acetate), R_f 0.61 (hexane–ethyl acetate, 5:1). IR spectrum: ν 3305 cm⁻¹ (NH). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.86 m (1H, 3-H), 2.19 d.q (1H, 3-H, $J_{2,3}$ = 8.5, ²J = 12.0, $J_{3a,3}$ = 8.9 Hz), 2.95 br.d.q (1H, 3a-H, $J_{3a,4}$ = 3.0, $J_{3a,9b}$ = 7.9, $J_{3a,3}$ = 8.9 Hz), 3.75 d.t (1H, 2-H, ²J = $J_{2,3}$ = 8.5, $J_{2,3}$ = 7.5 Hz), 3.80 q (1H, 2-H, ²J = $J_{2,3}$ = 8.5, $J_{2,3}$ = 4.6 Hz), 3.90 br.s (NH), 4.67 d (1H, 4-H, $J_{3a,4}$ = 3.0 Hz), 5.21 d (1H, 9b-H, $J_{3a,9b}$ = 7.9 Hz), 5.29 d (1H, 4'-H, $J_{4',3'}$ = 3.3 Hz), 6.27 d (1H, 3'-H, $J_{4',3'}$ = 3.3 Hz), 6.61 d.d (1H, 9-H, $J_{7,9}$ = 1.0, $J_{8,9}$ = 7.7 Hz), 6.83 d.t (1H, 7-H, $J_{7,9}$ = 1.0, $J_{7,8}$ = $J_{6,7}$ = 7.5 Hz), 7.09 d.t (1H, 8-H, $J_{7,8}$ = $J_{8,9}$ = 7.7, $J_{6,8}$ = 1.0 Hz), 7.37 br.d.d (1H, 6-H, $J_{6,7}$ = 7.5, $J_{6,8}$ = 1.0 Hz).

Mass spectrum, m/z (I_{rel} , %): 319 (100) [$M]^+$ (^{79}Br), 274 (79), 240 (30), 212 (31), 194 (22), 170 (41), 144 (17), 130 (46), 115 (18), 77 (23), 65 (13), 39 (15). Found, %: C 56.53; H 4.72; N 4.50. $\text{C}_{15}\text{H}_{14}\text{BrNO}_2$. Calculated, %: C 56.27; H 4.41; N 4.37. M 319.02.

(3aS*,4S,R*,9bS*)-4-(5-Nitrofuran-2-yl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (IIf) (a mixture of *cis* and *trans* isomers, 1:1). Yield 71%. Colorless crystals, mp 100–101°C (from hexane–ethyl acetate), R_f 0.32, 0.42 (hexane–ethyl acetate, 2:1). IR spectrum, ν , cm^{-1} : 3371, 3296 (NH). ^1H NMR spectrum (CDCl_3), δ , ppm: *cis* isomer: 1.89 m (1H, 3-H), 2.17 m (1H, 3-H), 3.04 d.q (1H, 3a-H, $J_{3a,4} = 2.7$, $J_{3a,9b} = 7.4$, $J_{3a,3} = 8.7$ Hz), 3.72 m (1H, 2-H), 3.79 q (1H, 2-H, $^2J = J_{2,3} = 8.1$ Hz), 4.26 br.s (NH), 4.77 d (1H, 4-H, $J_{3a,4} = 2.7$ Hz), 5.17 d (1H, 9b-H, $J_{3a,9b} = 7.4$ Hz), 6.55 d (1H, 3'-H, $J_{4',3'} = 3.4$ Hz), 6.65 d (1H, 6-H, $J_{6,7} = 7.7$ Hz), 6.87 t (1H, 8-H, $J_{7,8} = J_{8,9} = 7.7$ Hz), 7.13 t (1H, 7-H, $J_{6,7} = J_{7,8} = 7.7$ Hz), 7.30 d (1H, 4'-H, $J_{4',3'} = 3.4$ Hz), 7.36 d (1H, 9-H, $J_{8,9} = 7.7$ Hz); *trans* isomer: 1.89 m (1H, 3-H), 2.25 m (1H, 3-H), 2.68 m (1H, 3a-H), 3.86 q (1H, 2-H, $^2J = J_{2,3} = 8.7$ Hz), 4.02 m (1H, 2-H), 4.26 br.s (NH), 4.65 d (1H, 4-H, $J_{3a,4} = 5.4$ Hz), 4.10 d (1H, 9b-H, $J_{3a,9b} = 0.1$ Hz), 6.58 d (1H, 3'-H, $J_{4',3'} = 3.4$ Hz), 6.67 d (1H, 6-H, $J_{6,7} = 7.9$ Hz), 6.85 t (1H, 8-H, $J_{7,8} = J_{8,9} = 7.9$ Hz), 7.15 t (1H, 7-H, $J_{6,7} = J_{7,8} = 7.9$ Hz), 7.31 d (1H, 4'-H, $J_{4',3'} = 3.4$ Hz), 7.38 d (1H, 9-H, $J_{8,9} = 7.5$ Hz). Mass spectrum, m/z (I_{rel} , %): 286 (100) [$M]^+$, 241 (82), 180 (14), 170 (21), 158 (12), 144 (14), 130 (29), 115 (16), 77 (14), 65 (11), 51 (15), 39 (14). Found, %: C 62.64; H 4.77; N 9.95. $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_4$. Calculated, %: C 62.93; H 4.93; N 9.79. M 286.10.

Furyl-substituted quinolines **IIa**, **III**, and **IV** were reported previously [1, 2].

Cycloaddition of furoquinolines IIc–IId to maleic anhydride. *a.* A solution of 0.43 g (4.36 mmol) of maleic anhydride in 10 ml of toluene was added to a solution of 4.15 mmol of quinoline **IIc–IId** in 10 ml of toluene, heated to 0–5°C. The mixture was kept for 3 days at 0–5°C (TLC), and the precipitate was filtered off and washed with diethyl ether (2×15 ml). We thus isolated mixtures of *trans* and *cis* isomers of carboxylic acids **Vd** and **Ve** or pure *trans* isomer **Ve** as colorless crystalline substances. The isomer ratios are given in table.

b. A solution of 4.15 mmol of tetrahydroquinoline **IId** or **IHe** and 0.43 g (4.36 mmol) of maleic anhydride in 20 ml of toluene was heated for 2–10 h under reflux (TLC). The colorless crystalline product was filtered

off. We thus isolated *trans* isomers of carboxylic acids **Vd** and **Ve**.

(3aS*,9aS*,10R*,11S*,13aR*,13bS*,13cS*)-11,13a-Epoxy-7-hydroxy-9-oxo-1,2,9,9a,10,11,13b,13c-octahydro-3aH-furo[3,2-c]isoindolo[2,1-a]quinoline-10-carboxylic acid (Ve) (*trans* isomer). Yield 94%, mp 208–210°C (from *i*-PrOH–DMF). IR spectrum, ν , cm^{-1} : 1731 (COOH), 1649 ($\text{C}^{\text{9}}=\text{O}$). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 1.60 m (1H, 1-H), 2.15 m (1H, 1-H), 2.68 d (1H, 9a-H, $J_{9a,10} = 9.0$ Hz), 3.20 m (1H, 13c-H), 3.25 d (1H, 10-H, $J_{9a,10} = 9.0$ Hz), 3.72 m (1H, 2-H), 3.80 m (1H, 2-H), 4.51 d (1H, 13b-H, $J_{13b,13c} = 3.0$ Hz), 5.13 d (1H, 11-H, $J_{11,12} = 1.5$ Hz), 5.24 d (1H, 3a-H, $J_{3a,13c} = 8.6$ Hz), 6.55 d.d (1H, 12-H, $J_{11,12} = 1.5$, $J_{12,13} = 5.7$ Hz), 6.84 d.d (1H, 4-H, $J_{4,5} = 7.8$, $J_{4,6} = 0.9$ Hz), 6.91 d (1H, 13-H, $J_{12,13} = 5.7$ Hz), 6.91 br.d (1H, 6-H, $J_{5,6} = 7.8$ Hz), 7.16 t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.8$ Hz), 12.3 br.s (COOH). Mass spectrum, m/z (I_{rel} , %): 355 (7) [$M]^+$, 310 (3), 256 (62), 212 (40), 196 (5), 146 (28), 131 (33), 121 (52), 99 (67), 77 (100), 65 (46), 39 (45). Found, %: C 64.00; H 4.59; N 3.58. $\text{C}_{19}\text{H}_{17}\text{NO}_6$. Calculated, %: C 64.22; H 4.82; N 3.94. M 355.11.

(3aS*,9aS*,10R*,11S*,13aR*,13bS*,13cS*)-11,13a-Epoxy-11-methyl-9-oxo-1,2,9,9a,10,11,13b,13c-octahydro-3aH-furo[3,2-c]isoindolo[2,1-a]quinoline-10-carboxylic acid (VId) (*trans* isomer). Yield 62% (*b*), mp 178–180°C (from *i*-PrOH–DMF). IR spectrum, ν , cm^{-1} : 1724 (COOH), 1701 ($\text{C}^{\text{9}}=\text{O}$). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 1.53 s (3H, Me), 1.55 m (1H, 1-H), 2.10 m (1H, 1-H), 2.65 d (1H, 9a-H, $J_{9a,10} = 8.9$ Hz), 3.05 d (1H, 10-H, $J_{9a,10} = 8.9$ Hz), 3.11 m (1H, 13c-H), 3.67 m (1H, 2-H), 3.76 m (1H, 2-H), 4.44 d (1H, 13b-H, $J_{13b,13c} = 2.8$ Hz), 5.20 d (1H, 3a-H, $J_{3a,13c} = 8.3$ Hz), 6.37 d (1H, 12-H, $J_{12,13} = 5.6$ Hz), 6.89 d (1H, 13-H, $J_{12,13} = 5.6$ Hz), 6.91 br.d.d (1H, 6-H, $J_{4,6} = 1.5$, $J_{5,6} = 7.8$, $J_{6,7} = 8.1$ Hz), 7.14 d.t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.7$, $J_{5,7} = 1.1$ Hz), 7.35 d.d (1H, 4-H, $J_{4,5} = 7.7$, $J_{4,6} = 1.5$ Hz), 7.70 d.d (1H, 7-H, $J_{5,7} = 1.1$, $J_{6,7} = 8.1$ Hz). Mass spectrum, m/z (I_{rel} , %): 353 (10) [$M]^+$, 308 (18), 254 (100), 210 (99), 180 (21), 160 (34), 144 (23), 130 (29), 115 (21), 95 (28), 77 (29), 43 (64). Found, %: C 67.45; H 5.19; N 4.21. $\text{C}_{20}\text{H}_{19}\text{NO}_5$. Calculated, %: C 67.98; H 5.42; N 3.96. M 353.13.

(3aS*,9aS*,10R*,11S*,13aR*,13bS*,13cS*)-11-Bromo-1,13a-epoxy-9-oxo-1,2,9,9a,10,11,13b,13c-octahydro-3aH-furo[3,2-c]isoindolo[2,1-a]quinoline-10-carboxylic acid (VId) (*trans* isomer). Yield 75% (*b*), mp 204–206°C (from *i*-PrOH–DMF). IR spectrum, ν , cm^{-1} : 1732 (COOH), 1686 ($\text{C}^{\text{9}}=\text{O}$). ^1H NMR

spectrum ($\text{DMSO}-d_6$), δ , ppm: 1.49 m (1H, 1-H), 2.11 m (1H, 1-H), 3.11 d (1H, 9a-H, $J_{9a,10} = 8.9$ Hz), 3.13 m (1H, 13c-H), 3.27 d (1H, 10-H, $J_{9a,10} = 8.9$ Hz), 3.67 m (1H, 2-H), 3.75 m (1H, 2-H), 4.55 d (1H, 13b-H, $J_{13b,13c} = 2.9$ Hz), 5.29 d (1H, 3a-H, $J_{3a,13c} = 8.4$ Hz), 6.65 d (1H, 13-H, $J_{12,13} = 5.6$ Hz), 6.91 t (1H, 6-H, $J_{5,6} = J_{6,7} = 7.7$ Hz), 7.07 d (1H, 12-H, $J_{12,13} = 5.6$ Hz), 7.28 t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.7$ Hz), 7.36 d (1H, 4-H, $J_{4,5} = 7.7$ Hz), 7.70 d (1H, 7-H, $J_{6,7} = 7.7$ Hz), 11.8 br.s (COOH). Mass spectrum, m/z (I_{rel} , %): 417 (3) [$M]^+$ (^{79}Br), 318 (30), 293 (100), 264 (25), 248 (43), 236 (9), 115 (5), 44 (31). Found, %: C 54.31; H 3.65; N 3.17. $\text{C}_{19}\text{H}_{16}\text{BrNO}_5$. Calculated, %: C 54.56; H 3.86; N 3.35. M 417.02.

Isoindoloquinolines **Va**, **VI**, and **VII** were reported previously [1, 2].

Cycloaddition of furoquinolines IIc–IIe, III, and IV to acryloyl chloride. A solution of 4.15 mmol of tetrahydroquinoline **IIc–IIe**, **III**, or **IV**, 1.1 ml (12 mmol) of acryloyl chloride, and 2.4 ml (16.7 mmol) of triethylamine in 50 ml of benzene was heated for 2–4 h under reflux (TLC). The mixture was cooled and poured into 50 ml of water, the organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×40 ml). The extracts were combined with the organic phase, dried over anhydrous magnesium sulfate, and evaporated, and the residue was recrystallized from hexane–ethyl acetate to obtain mixtures of *trans*- and *cis*-isomeric isoindoloquinolines **VIIIc–VIIIe**, **IX**, and **X** as colorless crystalline substances.

(3aS*,9aS,R*,11R,S*,13aR,S*,13bS*,13cS*)-11,13a-Epoxy-7-hydroxy-1,2,10,11,13b,13c-hexahydro-3aH-furo[3,2-*c*]isoindolo[2,1-*a*]quinolin-9(9aH)-one (VIIIc) (mixture of *trans* and *cis* isomers at a ratio of 1:1). Yield 87%, mp 181–183°C (from hexane–ethyl acetate), R_f 0.35, 0.21 (hexane–ethyl acetate, 1:2). IR spectrum: ν 1696 cm^{-1} (C=O). ^1H NMR spectrum (CDCl_3), δ , ppm: *trans* isomer: 1.76 d.d (1H, *endo*-10-H, $J_{9a,\text{endo-10}} = 9.2$, $^2J = 12.1$ Hz), 1.90 m (1H, 1-H), 2.05 m (1H, 1-H), 2.34 d.d.d (1H, *exo*-10-H, $J_{9a,\text{exo-10}} = 3.9$, $J_{\text{exo-10,11}} = 4.8$, $^2J = 12.1$ Hz), 2.76 d.d (1H, 9a-H, $J_{9a,\text{exo-10}} = 3.9$, $J_{9a,\text{endo-10}} = 9.2$ Hz), 3.21 m (1H, 13c-H), 3.89–4.03 m (2H, 2-H), 4.47 d (1H, 13b-H, $J_{13b,13c} = 3.4$ Hz), 5.17 d.d (1H, 11-H, $J_{\text{exo-10,11}} = 4.8$, $J_{11,12} = 1.5$ Hz), 5.37 d (1H, 3a-H, $J_{3a,13c} = 8.2$ Hz), 6.47 d.d (1H, 12-H, $J_{11,12} = 1.5$, $J_{12,13} = 5.8$ Hz), 6.57 d (1H, 13-H, $J_{12,13} = 5.8$ Hz), 6.98 d.d (1H, 6-H, $J_{5,6} = 7.7$, $J_{4,6} = 1.5$ Hz), 7.21 t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.7$ Hz), 7.22 d.d (1H, 4-H, $J_{4,5} = 7.7$,

$J_{4,6} = 1.5$ Hz), 9.45 s (OH); *cis* isomer: 1.77 d.d (1H, *endo*-10-H, $J_{9a,\text{endo-10}} = 9.2$, $^2J = 11.6$ Hz), 1.90 m (1H, 1-H), 2.13 m (1H, 1-H), 2.17 d.d.d (1H, *exo*-10-H, $J_{9a,\text{exo-10}} = 3.9$, $J_{\text{exo-10,11}} = 4.4$, $^2J = 11.6$ Hz), 2.55 d.d (1H, 9a-H, $J_{9a,\text{exo-10}} = 3.9$, $J_{9a,\text{endo-10}} = 9.2$ Hz), 3.15 m (1H, 13c-H), 3.89–4.03 m (2H, 2-H), 4.52 d (1H, 13b-H, $J_{13b,13c} = 2.9$ Hz), 5.14 d.d (1H, 11-H, $J_{\text{exo-10,11}} = 4.4$, $J_{11,12} = 1.5$ Hz), 5.35 d (1H, 3a-H, $J_{3a,13c} = 8.2$ Hz), 6.53 d.d (1H, 12-H, $J_{11,12} = 1.5$, $J_{12,13} = 5.8$ Hz), 6.58 d (1H, 13-H, $J_{12,13} = 5.8$ Hz), 7.00 d.d (1H, 6-H, $J_{5,6} = 7.7$, $J_{4,6} = 1.5$ Hz), 7.29 t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.7$ Hz), 7.36 d.d (1H, 4-H, $J_{4,5} = 7.7$, $J_{4,6} = 1.5$ Hz), 9.45 s (OH). Mass spectrum, m/z (I_{rel} , %): 311 (31) [$M]^+$, 266 (34), 256 (27), 212 (100), 196 (17), 160 (10), 121 (47), 103 (67), 94 (60), 80 (64), 59 (66). Found, %: C 69.29; H 5.22; N 4.34. $\text{C}_{18}\text{H}_{17}\text{NO}_4$. Calculated, %: C 69.44; H 5.50; N 4.50. M 311.12.

(3aS*,9aS,R*,11R,S*,13aR,S*,13bS*,13cS*)-11,13a-Epoxy-11-methyl-1,2,10,11,13b,13c-hexahydro-3aH-furo[3,2-*c*]isoindolo[2,1-*a*]quinolin-9(9aH)-one (VIIId) (mixture of *trans* and *cis* isomers at a ratio of 1:1). Yield 87%, mp 157–158°C (from hexane–ethyl acetate), R_f 0.62, 0.91 (hexane–ethyl acetate, 1:1). IR spectrum: ν 1691 cm^{-1} (C=O). ^1H NMR spectrum (CDCl_3), δ , ppm: *trans* isomer: 1.69 s (3H, Me), 1.80 d.d (1H, *endo*-10-H, $J_{9a,\text{endo-10}} = 9.0$, $^2J = 11.8$ Hz), 1.86 m (1H, 1-H), 2.07 d.d (1H, *exo*-10-H, $J_{9a,\text{exo-10}} = 3.5$, $^2J = 11.8$ Hz), 2.65 m (1H, 1-H), 2.89 m (1H, 13c-H), 3.72 d.d (1H, 9a-H, $J_{9a,\text{exo-10}} = 3.5$, $J_{9a,\text{endo-10}} = 9.0$ Hz), 3.86–3.95 m (2H, 2-H), 4.42 d (1H, 13b-H, $J_{13b,13c} = 2.7$ Hz), 5.36 d (1H, 3a-H, $J_{3a,13c} = 8.2$ Hz), 6.33 d (1H, 13-H, $J_{12,13} = 5.7$ Hz), 6.54 d (1H, 12-H, $J_{12,13} = 5.7$ Hz), 7.17 d.t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.7$, $J_{5,7} = 1.1$ Hz), 7.32 d.d (1H, 6-H, $J_{5,6} = 7.7$, $J_{6,7} = 8.1$ Hz), 7.42 br.d (1H, 4-H, $J_{4,5} = 7.7$ Hz), 8.03 d.d (1H, 7-H, $J_{5,7} = 1.1$, $J_{6,7} = 8.1$ Hz); *cis* isomer: 1.64 s (3H, Me), 1.71 d.d (1H, *endo*-10-H, $J_{9a,\text{endo-10}} = 8.7$, $^2J = 11.8$ Hz), 1.86 m (1H, 1-H), 1.99 d.d (1H, *exo*-10-H, $J_{9a,\text{exo-10}} = 3.6$, $^2J = 11.8$ Hz), 2.70 m (1H, 1-H), 3.11 m (1H, 13c-H), 3.66 d.d (1H, 9a-H, $J_{9a,\text{exo-10}} = 3.6$, $J_{9a,\text{endo-10}} = 8.7$ Hz), 3.84 m (2H, 2-H), 4.70 d (1H, 13b-H, $J_{13b,13c} = 2.5$ Hz), 5.24 d (1H, 3a-H, $J_{3a,13c} = 7.2$ Hz), 6.30 d (1H, 13-H, $J_{12,13} = 5.7$ Hz), 6.44 d (1H, 12-H, $J_{12,13} = 5.7$ Hz), 7.11 d.t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.7$, $J_{5,7} = 1.1$ Hz), 7.24 d.d (1H, 6-H, $J_{5,6} = 7.7$, $J_{6,7} = 8.4$ Hz), 7.48 br.d (1H, 4-H, $J_{4,5} = 7.7$ Hz), 8.66 d.d (1H, 7-H, $J_{5,7} = 1.1$, $J_{6,7} = 8.4$ Hz). Mass spectrum, m/z (I_{rel} , %): 309 (18) [$M]^+$, 264 (18), 210 (100), 158 (17), 130 (11), 115 (18), 91 (17), 77 (25), 55 (73), 43 (52). Found, %: C 73.54; H 6.00; N 4.79. $\text{C}_{19}\text{H}_{19}\text{NO}_3$. Calculated, %: C 73.77; H 6.19; N 4.53. M 309.14.

(3aS*,9aS,R*,11R,S*,13aR,S*,13bS*,13cS*)-11-Bromo-11,13a-epoxy-1,2,10,11,13b,13c-hexahydro-3aH-furo[3,2-c]isoindolo[2,1-a]quinolin-9(9aH)-one (VIIIe) (mixture of *trans* and *cis* isomers, 1:1). Yield 44%, mp 171–173°C (from hexane–ethyl acetate), R_f 0.62, 0.79 (hexane–ethyl acetate, 1:1). IR spectrum: ν 1701 cm⁻¹ ($C=O$). ¹H NMR spectrum ($CDCl_3$), δ , ppm: *trans* isomer: 1.88 m (1H, 1-H), 2.01 m (1H, 1-H), 2.31 d.d (1H, *endo*-10-H, $J_{9a,endo-10} = 8.6$, $^2J = 11.9$ Hz), 2.65 d.d (1H, *exo*-10-H, $J_{9a,exo-10} = 3.6$, $^2J = 11.9$ Hz), 2.77 d.d (1H, 9a-H, $J_{9a,exo-10} = 3.6$, $J_{9a,endo-10} = 8.6$ Hz), 3.09 m (1H, 13c-H), 3.84 m (1H, 2-H), 3.89 m (1H, 2-H), 4.45 d (1H, 13b-H, $J_{13b,13c} = 2.9$ Hz), 5.35 br.d (1H, 3a-H, $J_{3a,13c} = 8.3$ Hz), 6.52 d (1H, 13-H, $J_{12,13} = 5.7$ Hz), 6.55 d (1H, 12-H, $J_{12,13} = 5.7$ Hz), 7.17 d.t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.7$, $J_{5,7} = 1.2$ Hz), 7.30 br.d.d (1H, 6-H, $J_{5,6} = 7.7$, $J_{6,7} = 7.9$ Hz), 7.41 d.d (1H, 4-H, $J_{4,5} = 7.7$, $J_{4,6} = 1.4$ Hz), 8.01 d.d (1H, 7-H, $J_{5,7} = 1.2$, $J_{6,7} = 7.9$ Hz); *cis* isomer: 1.80 m (1H, 1-H), 2.19 m (1H, 1-H), 2.24 d.d (1H, *endo*-10-H, $J_{9a,endo-10} = 8.5$, $^2J = 12.1$ Hz), 2.61 d.d (1H, *exo*-10-H, $J_{9a,exo-10} = 3.6$, $^2J = 12.1$ Hz), 2.80 d.d (1H, 9a-H, $J_{9a,exo-10} = 3.6$, $J_{9a,endo-10} = 8.5$ Hz), 2.89 m (1H, 13c-H), 3.66 m (1H, 2-H), 3.84 m (1H, 2-H), 4.72 d (1H, 13b-H, $J_{13b,13c} = 2.7$ Hz), 5.23 br.d (1H, 3a-H, $J_{3a,13c} = 7.1$ Hz), 6.48 d (1H, 13-H, $J_{12,13} = 5.7$ Hz), 6.51 d (1H, 12-H, $J_{12,13} = 5.7$ Hz), 7.12 d.t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.6$, $J_{5,7} = 1.1$ Hz), 7.28 br.d.d (1H, 6-H, $J_{5,6} = 7.6$, $J_{6,7} = 8.0$ Hz), 7.48 br.d (1H, 4-H, $J_{4,5} = 7.6$ Hz), 8.61 d.d (1H, 7-H, $J_{5,7} = 1.1$, $J_{6,7} = 8.0$ Hz). Mass spectrum, m/z (I_{rel} , %): 373 (25) [$M]^+$ (⁷⁹Br), 328 (14), 294 (37), 274 (100), 194 (35), 182 (33), 172 (43), 158 (81), 130 (31), 115 (26), 91 (56), 77 (43), 55 (93), 43 (70). Found, %: C 57.92; H 4.48; N 3.98. $C_{18}H_{16}BrNO_3$. Calculated, %: C 57.77; H 4.31; N 3.74. M 373.03.

Isoindoloquinolines **VIIIa**, **IX**, and **X** were reported previously [1, 2].

(3aS*,9aS*,10R*,11S*,13aR*,13bS*,13cS*)-11,13a-Epoxy-10-methyl-9-oxo-1,2,9,9a,10,11,13b,13c-octahydro-3aH-furo[3,2-c]isoindolo[2,1-a]quinoline-10-carboxylic acid (XI). A solution of 1 g (0.04 mol) of compound **IIa** and 16.2 ml (0.18 mol) of citraconic anhydride in 20 ml of *o*-xylene was heated for 6 h, the progress of the reaction being monitored by TLC. The solvent was distilled off, and the precipitate was filtered off and recrystallized from propan-2-ol–DMF. Yield 19%, colorless crystals, mp 140°C (from *i*-PrOH–DMF). IR spectrum, ν , cm⁻¹: 1721 (COOH), 1659 ($C^2=O$). ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 1.12 s (3H, Me), 1.52 m (1H, 1-H), 2.10 m (1H, 1-H), 3.12 m (1H, 13c-H), 3.67 m (1H, 2-H), 3.75 m (1H,

2-H), 4.40 d (1H, 13b-H, $J_{13b,13c} = 2.8$ Hz), 4.96 d (1H, 11-H, $J_{11,12} = 1.7$ Hz), 5.27 d (1H, 3a-H, $J_{3a,13c} = 8.3$ Hz), 6.58 d.d (1H, 12-H, $J_{11,12} = 1.7$, $J_{12,13} = 5.7$ Hz), 6.92 d (1H, 13-H, $J_{12,13} = 5.7$ Hz), 7.14 d.t (1H, 6-H, $J_{4,6} = 1.3$, $J_{5,6} = J_{6,7} = 7.6$ Hz), 7.26 d.t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.6$, $J_{5,7} = 1.3$ Hz), 7.35 d.d (1H, 4-H, $J_{4,5} = 7.7$, $J_{4,6} = 1.3$ Hz), 7.72 d.d (1H, 7-H, $J_{5,7} = 1.3$, $J_{6,7} = 7.6$ Hz). ¹³C NMR spectrum (DMSO-*d*₆), δ _C, ppm: 22.3 q (Me, $J = 128.0$ Hz), 24.8 t (C^1 , $J = 131.0$ Hz), 39.3 d (C^{13c} , $J = 135.5$ Hz), 51.0 s (C^{10}), 58.7 d (C^{13b} , $J = 145.0$ Hz), 59.1 d (C^{9a} , $J = 137.5$ Hz), 67.2 t (C^2 , $J = 147.0$ Hz), 76.0 d (C^{3a} , $J = 152.0$ Hz), 84.3 d (C^{11} , $J = 166.5$ Hz), 90.5 s (C^{13a}), 120.5 d (C^7 , $J = 164.5$ Hz), 124.8 d (C^5 , $J = 161.0$ Hz), 127.7 d (C^6 , $J = 161.5$ Hz), 128.7 s (C^{3b}), 130.1 d (C^4 , $J = 159.0$ Hz), 134.8 d (C^{13} , $J = 177.8$ Hz), 135.1 s (C^{7a}), 137.1 s (C^{12} , $J = 177.0$ Hz), 169.5 s (C^9), 174.6 s (COOH). Mass spectrum, m/z (I_{rel} , %): 353 (1) [$M]^+$, 241 (21), 196 (45), 130 (22), 115 (16), 91 (24), 77 (36), 68 (42), 39 (100). Found, %: C 67.55; H 5.76; N 4.21. $C_{20}H_{19}NO_5$. Calculated, %: C 67.98; H 5.42; N 3.96. M 353.13.

(3aS*,9aR*,10S*,11S*,13aS*,13bS*,13cS*)-9a,10-Dibromo-11,13a-epoxy-9-oxo-1,2,9,9a,10,11,13b,13c-octahydro-3aH-furo[3,2-c]isoindolo[2,1-a]quinoline-10-carboxylic acid (XII). A solution of 0.9 g (3.50 mmol) of dibromomaleic anhydride in 10 ml of toluene was added to a solution of 0.8 g (3.20 mmol) of compound **IIa** in 10 ml of toluene, and the mixture was stirred for 3 days at room temperature (TLC). The precipitate was filtered off and washed with diethyl ether (2×15 ml). Yield 32%, colorless crystals, mp 174°C (from *i*-PrOH–DMF). IR spectrum, ν , cm⁻¹: 1723 (COOH), 1702 ($C^2=O$). ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 1.60 m (1H, 1-H), 1.93 m (1H, 1-H), 2.90 m (1H, 13c-H), 3.49 m (1H, 2-H), 3.74 m (1H, 2-H), 5.04 d (1H, 13b-H, $J_{13b,13c} = 2.6$ Hz), 5.26 d (1H, 3a-H, $J_{3a,13c} = 6.8$ Hz), 5.61 d (1H, 11-H, $J_{11,12} = 1.8$ Hz), 6.76 m (2H, 12-H, 13-H), 7.17 d.t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.3$, $J_{5,7} = 1.3$ Hz), 7.28 d.d (1H, 6-H, $J_{5,6} = 7.3$, $J_{6,7} = 8.3$ Hz), 7.42 br.d (1H, 4-H, $J_{4,5} = 7.3$ Hz), 8.44 d.d (1H, 7-H, $J_{5,7} = 1.3$, $J_{6,7} = 8.3$ Hz). Mass spectrum, m/z (I_{rel} , %): 497 (2) [$M]^+$ (⁷⁹Br), 371 (11), 325 (26), 293 (21), 241 (67), 220 (33), 196 (92), 167(61), 143 (47), 131 (100), 115 (70), 80 (96), 59 (68). Found, %: C 45.73; H 2.88; N 2.66. $C_{19}H_{15}Br_2NO_5$. Calculated, %: C 45.90; H 3.04; N 2.82. M 494.93.

Cycloaddition of furoquinoline **IIa to cinnamoyl and methacryloyl chlorides.** A solution of 1 g (4.15 mmol) of tetrahydroquinoline **IIa**, 2 g (12 mmol)

of cinnamoyl chloride (in the synthesis of compound **XIII**) or 1.2 ml (12 mmol) of methacryloyl chloride (in the synthesis of **XIV**), and 2.4 ml (16.7 mmol) of triethylamine in 50 ml of benzene was heated for 4 h under reflux (TLC). The mixture was cooled and poured into 50 ml of water, the organic layer was separated, the aqueous layer was extracted with ethyl acetate (3×40 ml), the extracts were combined with the organic phase, dried over anhydrous magnesium sulfate, and evaporated, and the residue was recrystallized from hexane–ethyl acetate.

(3aS*,9aS*,10R*,11S*,13aR*,13bS*,13cS*)-11,13a-Epoxy-10-phenyl-1,2,10,11,13b,13c-hexahydro-3aH-furo[3,2-*c*]isoindolo[2,1-*a*]quinolin-9(9aH)-one (XIII). Yield 37%, colorless crystals, mp 174°C (from hexane–ethyl acetate), R_f 0.83 (hexane–ethyl acetate, 1:1). IR spectrum: ν 1693 cm⁻¹ (C=O). ¹H NMR spectrum (CDCl_3), δ , ppm: 1.96 m (1H, 1-H), 2.18 m (1H, 1-H), 2.93 m (1H, 13c-H), 2.93 d (1H, 9a-H, $J_{9a,10} = 4.3$ Hz), 3.71 m (1H, 2-H), 3.88 m (1H, 2-H), 3.92 t (1H, 10-H, $J_{9a,10} = J_{10,11} = 4.3$ Hz), 4.81 d (1H, 13b-H, $J_{13b,13c} = 2.2$ Hz), 5.29 d.d (1H, 11-H, $J_{11,12} = 1.6$, $J_{10,11} = 4.3$ Hz), 5.30 br.s (1H, 3a-H), 6.41 d.d (1H, 12-H, $J_{11,12} = 1.6$, $J_{12,13} = 5.6$ Hz), 6.64 d (1H, 13-H, $J_{12,13} = 5.6$ Hz), 7.21–7.32 m (7H, H_{arom}), 7.52 d (1H, 4-H, $J_{4,5} = 7.7$ Hz), 8.69 d (1H, 7-H, $J_{6,7} = 8.1$ Hz). Mass spectrum, m/z (I_{rel} , %): 371 (32) [$M]^+$, 326 (15), 240 (40), 213 (14), 196 (82), 154 (16), 131 (100), 103 (67), 77 (24), 43 (64), 33 (34). Found, %: C 77.93; H 5.98; N 3.86. $C_{24}\text{H}_{21}\text{NO}_3$. Calculated, %: C 77.61; H 5.70; N 3.77. M 371.15.

(3aS*,9aS*,11R*,13aR*,13bS*,13cS*)-11,13a-Epoxy-9a-methyl-1,2,10,11,13b,13c-hexahydro-3aH-furo[3,2-*c*]isoindolo[2,1-*a*]quinolin-9(9aH)-one (XIV). Yield 55%, colorless crystals, mp 148°C (from hexane–ethyl acetate), R_f 0.50 (hexane–ethyl acetate, 2:1). IR spectrum: ν 1692 cm⁻¹ (C=O). ¹H NMR spectrum (CDCl_3), δ , ppm: 1.06 s (3H, Me), 1.10 d (1H, endo-10-H, $J = 11.7$ Hz), 1.84 m (1H, 1-H), 2.49 d.d (1H, exo-10-H, $J_{\text{exo}-10,11} = 4.7$, $J = 11.7$ Hz), 2.05 m (1H, 1-H), 2.82 m (1H, 13c-H), 3.62 m (1H, 2-H), 3.78 m (1H, 2-H), 4.62 d (1H, 13b-H, $J_{13b,13c} = 2.7$ Hz), 4.97 d.d (1H, 11-H, $J_{11,12} = 1.6$, $J_{\text{exo}-10,11} = 4.7$ Hz), 5.21 d (1H, 3a-H, $J_{3a,13c} = 7.0$ Hz), 6.39 d (1H, 13-H, $J_{12,13} = 5.8$ Hz), 6.48 d.d (1H, 12-H, $J_{11,12} = 1.6$, $J_{12,13} = 5.7$ Hz), 7.06 d.t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.6$, $J_{5,7} = 0.8$ Hz), 7.22 d.d.d (1H, 6-H, $J_{4,6} = 1.0$, $J_{5,6} = 7.6$, $J_{6,7} = 8.4$ Hz), 7.43 br.d (1H, 4-H, $J_{4,5} = 7.6$ Hz), 8.61 d.d (1H, 7-H, $J_{5,7} = 0.8$, $J_{6,7} = 8.4$ Hz). Mass spectrum, m/z (I_{rel} , %): 309 (7) [$M]^+$, 264 (5), 240 (3), 180 (3), 15 (5), 91 (7), 69 (51), 41 (100). Found, %:

C 73.89; H 6.05; N 4.89. $C_{19}\text{H}_{19}\text{NO}_3$. Calculated, %: C 73.77; H 6.19; N 4.53. M 309.14.

Esterification of epoxyisoindoloquinolinecarboxylic acids **Vd, **VI**, **VII**, and **XI** (general procedure).** A mixture of 4.4 mmol of *trans*-isomeric acid **Vd**, **VI**, or **XI** or *cis*-acid **VII**, 30 ml of methanol, and one drop of sulfuric acid was heated for 2–6 h under reflux. The solution was poured into 50 ml of water and extracted with chloroform (3×50 ml), the extract was dried over anhydrous magnesium sulfate and evaporated, and the residue was recrystallized from ethyl-acetate–hexane to isolate methyl esters **XVd** and **XVI–XVIII** as colorless crystalline substances.

Methyl (3aS*,9aS,R*,10RS*,11SR*,13aRS*,-13bS*,13cS*)-11,13a-Epoxy-11-methyl-9-oxo-1,2,9,-9a,10,11,13b,13c-octahydro-3aH-furo[3,2-*c*]isoindolo[2,1-*a*]quinoline-10-carboxylate (XVd) (mixture of *trans* and *cis* isomers). Yield 80%, mp 187–189°C (from hexane–ethyl acetate), R_f 0.47 (ethanol–ethyl acetate, 1:8). IR spectrum, ν , cm⁻¹: 1730 (COOMe), 1702 (C=O). ¹H NMR spectrum (CDCl_3), δ , ppm: *trans* isomer: 1.68 s (3H, Me), 1.81 m (1H, 1-H), 2.05 m (1H, 1-H), 2.90 d (1H, 9a-H, $J_{9a,10} = 8.8$ Hz), 2.99 d (1H, 10-H, $J_{9a,10} = 8.8$ Hz), 3.13 m (1H, 13c-H), 3.84 s (3H, OMe), 3.86 m (1H, 2-H), 3.93 m (1H, 2-H), 4.57 d (1H, 13b-H, $J_{13b,13c} = 2.6$ Hz), 5.37 d (1H, 3a-H, $J_{3a,13c} = 8.2$ Hz), 6.34 d (1H, 12-H, $J_{12,13} = 5.6$ Hz), 6.69 d (1H, 13-H, $J_{12,13} = 5.6$ Hz), 7.18 br.t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.5$ Hz), 7.30 d.d.d (1H, 6-H, $J_{4,6} = 1.0$, $J_{5,6} = 7.5$, $J_{6,7} = 8.2$ Hz), 7.43 br.d (1H, 4-H, $J_{4,5} = 7.5$ Hz), 7.96 d (1H, 7-H, $J_{6,7} = 8.2$ Hz); *cis* isomer: 1.66 s (3H, Me), 2.05 m (1H, 1-H), 2.25 m (1H, 1-H), 2.82 d (1H, 9a-H, $J_{9a,10} = 8.8$ Hz), 2.93 m (1H, 13c-H), 3.04 d (1H, 10-H, $J_{9a,10} = 8.8$ Hz), 3.77 s (3H, OMe), 3.66 m (2H, 2-H), 4.69 d (1H, 13b-H, $J_{13b,13c} = 2.3$ Hz), 5.28 d (1H, 3a-H, $J_{3a,13c} = 7.2$ Hz), 6.28 d (1H, 12-H, $J_{12,13} = 5.6$ Hz), 6.61 d (1H, 13-H, $J_{12,13} = 5.6$ Hz), 7.13 br.t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.5$ Hz), 7.26 d.d.d (1H, 6-H, $J_{4,6} = 0.9$, $J_{5,6} = 7.5$, $J_{6,7} = 8.2$ Hz), 7.48 br.d (1H, 4-H, $J_{4,5} = 7.5$ Hz), 8.65 d (1H, 7-H, $J_{6,7} = 8.2$ Hz). Mass spectrum, m/z (I_{rel} , %): 367 (17) [$M]^+$, 322 (16), 254 (100), 210 (37), 180 (4), 135 (6), 13 (9), 43 (6). Found, %: C 68.80; H 5.58; N 3.65. $C_{21}\text{H}_{21}\text{NO}_5$. Calculated, %: C 68.65; H 5.76; N 3.81. M 367.14.

Methyl (3aS*,9aS*,10R*,11S*,13aR*,13bS*,13cS*)-11,13a-epoxy-10-methyl-9-oxo-1,2,9,9a,-10,11,13b,13c-octahydro-3aH-furo[3,2-*c*]isoindolo[2,1-*a*]quinoline-10-carboxylate (XVI) (*trans* isomer). Yield 46%, mp 220°C (from hexane–ethyl ace-

tate), R_f 0.50 (hexane–ethyl acetate, 2:1). IR spectrum, ν , cm^{-1} : 1721 (COOMe), 1687 ($\text{C}^9=\text{O}$). ^1H NMR spectrum (CDCl_3), δ , ppm: 1.33 s (3H, Me), 1.78 m (1H, 1-H), 2.04 m (1H, 1-H), 3.13 m (1H, 13c-H), 3.82–3.92 m (2H, 2-H), 4.48 d (1H, 13b-H, $J_{13b,13c} = 3.1$ Hz), 5.05 d (1H, 11-H, $J_{11,12} = 1.9$ Hz), 5.36 d (1H, 3a-H, $J_{3a,13c} = 8.1$ Hz), 6.58 d.d (1H, 12-H, $J_{11,12} = 1.9$, $J_{12,13} = 5.6$ Hz), 6.70 d (1H, 13-H, $J_{12,13} = 5.6$ Hz), 7.30 d.d.d (1H, 6-H, $J_{4,6} = 1.2$, $J_{5,6} = 7.5$, $J_{6,7} = 8.1$ Hz), 7.17 d.t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.5$, $J_{5,7} = 1.2$ Hz), 7.42 br.d (1H, 4-H, $J_{4,5} = 7.5$, $J_{4,6} = 1.2$ Hz), 7.97 d.d (1H, 7-H, $J_{5,7} = 1.2$, $J_{6,7} = 8.1$ Hz). Mass spectrum, m/z (I_{rel} , %): 367 (9) [$M]^+$, 322 (7), 240 (100), 196 (43), 127 (52), 101 (26), 83 (14), 59 (23), 43 (47). Found, %: C 68.92; H 5.53; N 3.56. $\text{C}_{21}\text{H}_{21}\text{NO}_5$. Calculated, %: C 68.65; H 5.76; N 3.81. M 367.14.

Methyl (4aS*,10aS*,11R*,12S*,14aR*,14bS*,14cS*)-12,14a-Epoxy-10-oxo-2,3,10,10a,11,12,14b,14c-octahydro-1H,4aH-pyrano[3,2-c]isoindolo[2,1-a]quinoline-11-carboxylate (XVII) (*trans* isomer). Yield 93%, mp 256°C (from hexane–ethyl acetate), R_f 0.50 (hexane–ethyl acetate, 1:4). IR spectrum, ν , cm^{-1} : 1690 ($\text{C}^{10}=\text{O}$), 1736 (COOMe). ^1H NMR spectrum (CDCl_3), δ , ppm: 1.45 m (1H, 1-H), 1.53 m (1H, 1-H), 1.64 m (1H, 2-H), 1.81 m (1H, 2-H), 2.60 m (1H, 14c-H), 2.83 d (1H, 11-H, $J_{10a,11} = 9.1$ Hz), 2.85 d (1H, 10a-H, $J_{10a,11} = 9.1$ Hz), 3.31 m (1H, 3-H), 3.65 m (1H, 3-H), 3.81 s (3H, OCH₃), 4.37 br.d (1H, 14b-H, $J_{14b,14c} = 1.9$ Hz), 5.15 br.d (1H, 4a-H, $J_{4a,14c} = 5.9$ Hz), 5.18 d (1H, 12-H, $J_{12,13} = 1.7$ Hz), 6.53 d.d (1H, 13-H, $J_{13,14} = 5.7$, $J_{12,13} = 1.7$ Hz), 6.66 d (1H, 14-H, $J_{13,14} = 5.7$ Hz), 7.17 br.d.t (1H, 6-H, $J_{6,7} = 7.5$, $J_{5,6} = 7.7$, $J_{6,8} = 1.1$ Hz), 7.28 d.d.d (1H, 7-H, $J_{7,8} = 8.1$, $J_{6,7} = 7.5$, $J_{5,7} = 0.9$ Hz), 7.54 d.d (1H, 5-H, $J_{5,6} = 7.7$, $J_{5,7} = 0.9$ Hz), 8.10 d.d (1H, 8-H, $J_{7,8} = 8.1$, $J_{6,8} = 1.1$ Hz). Mass spectrum, m/z (I_{rel} , %): 367 (33) [$M]^+$, 308 (11), 254 (100), 210 (11), 196 (37), 167 (6), 113 (15), 77 (6), 59 (5). Found, %: C 68.99; H 5.91; N 3.66. $\text{C}_{21}\text{H}_{11}\text{NO}_5$. Calculated, %: C 68.65; H 5.76; N 3.81. M 367.40.

Methyl (5S*,6aS*,6bS*,9R*,10S*,10aR*)-6b,9-Epoxy-5-ethoxy-11-oxo-6,6a,9,10,10a,11-hexahydro-5H-isoindolo[2,1-a]quinoline-10-carboxylate (XVIII) (*cis* isomer). Yield 78%, mp 154–156°C (from hexane–ethyl acetate), R_f 0.65 (hexane–ethyl acetate, 6:1). IR spectrum, ν , cm^{-1} : 1691 ($\text{C}^{11}=\text{O}$), 1739 (COOMe). ^1H NMR spectrum (CDCl_3), δ , ppm: 1.30 t (3H, CH₂CH₃, $^3J = 6.9$ Hz), 2.27 d.t (1H, 6-H_{ax}, $J_{5,6-ax} = 11.5$, $J_{6a,6-ax} = ^2J = 12.5$ Hz), 2.47 d.d.d (1H, 6-H_{eq}, $J_{5,6-eq} = 5.9$, $J_{6a,6-eq} = 2.6$, $^2J = 12.5$ Hz), 2.82 d (1H, 10a-H, $J_{10a,endo-10} = 9.2$ Hz), 3.03 d (1H, *endo*-

10-H, $J_{10a,endo-10} = 9.2$ Hz), 3.70 d.q and 3.59 (1H each, OCH₂, $^2J = 9.0$, $^3J = 6.9$ Hz), 3.81 s (3H, OMe), 4.54 d.d (1H, 6a-H, $J_{6a,6-ax} = 12.5$, $J_{6a,6-eq} = 2.6$ Hz), 4.83 d.d (1H, 5-H, $J_{5,6-ax} = 11.5$, $J_{5,6-eq} = 5.9$ Hz), 5.26 d (1H, 9-H, $J_{8,9} = 1.3$ Hz), 6.56 m (2H, 7-H, 8-H), 7.12 d.t (1H, 3-H, $J_{2,3} = J_{3,4} = 7.7$, $J_{1,3} = 0.8$ Hz), 7.26 d.d.d (1H, 2-H, $J_{1,2} = 8.4$, $J_{2,3} = 7.7$, $J_{2,4} = 0.8$ Hz), 7.58 d (1H, 4-H, $J_{3,4} = 7.7$ Hz), 8.63 d.d (1H, 1-H, $J_{1,2} = 8.4$, $J_{1,3} = 0.8$ Hz). Mass spectrum, m/z (I_{rel} , %): 355 (24) [$M]^+$, 242 (43), 196 (100), 168 (7), 130 (12), 113 (17), 77 (6), 65 (5). Found, %: C 67.72; H 5.88; N 3.76. $\text{C}_{20}\text{H}_{21}\text{NO}_5$. Calculated, %: C 67.59; H 5.96; N 3.94. M 355.38.

trans- and *cis*-Isomeric methyl esters **XVa** were reported previously [1, 2].

Epoxidation of compounds X, XIII, XIV, *trans*-XVa, *trans*-XVd, *trans*-XVI, *trans*-XVII, and *cis*-XVIII (general procedure). A solution of 5 mmol of isoindoloquinoline **X**, **XIII**, **XIV**, *trans*-**XVa**, *trans*-**XVd**, *trans*-**XVI**, *trans*-**XVII**, or *cis*-**XVIII** and 2.19 g (12.7 mmol) of *m*-chloroperoxybenzoic acid in 50 ml of methylene chloride was stirred for 2 h, the progress of the reaction being monitored by TLC. The mixture was then poured into 50 ml of water and made weakly alkaline by adding a saturated solution of sodium carbonate. The organic layer was separated, the aqueous phase was extracted with methylene chloride (3 × 50 ml), the extracts were combined with the organic phase, dried over anhydrous magnesium sulfate, and filtered. The solvent was distilled off, and the residue was recrystallized from ethyl acetate–hexane.

Methyl (3aS*,9aS*,10R*,11R*,11aR*,12aR*,12bR*,12cS*,12dS*)-11,12b-epoxy-9-oxo-1,2,9,9a-,10,11,11a,12a,12c,12d-decahydro-3aH-furo[3,2-c]-oxirano[6,7]isoindolo[2,1-a]quinoline-10-carboxylate (XIXa). Yield 53%, colorless crystals, mp 192°C (from hexane–ethyl acetate), R_f 0.20 (hexane–ethyl acetate, 1:1). IR spectrum, ν , cm^{-1} : 1725 (COOMe), 1696 ($\text{C}^9=\text{O}$). ^1H NMR spectrum (CDCl_3), δ , ppm: 1.76 m (1H, 1-H), 2.10 m (1H, 1-H), 3.04 d (1H, 10-H, $J_{9a,10} = 9.4$ Hz), 3.14 d (1H, 9a-H, $J_{9a,10} = 9.4$ Hz), 3.14 m (1H, 12d-H), 3.49 d (1H, 11a-H, $J_{11a,12a} = 3.3$ Hz), 3.56 d (1H, 12a-H, $J_{11a,12a} = 3.3$ Hz), 3.80 s (3H, OMe), 3.81 m (1H, 2-H), 3.93 m (1H, 2-H), 4.52 d (1H, 12c-H, $J_{12c,12d} = 2.5$ Hz), 4.79 s (1H, 11-H), 5.36 d (1H, 3a-H, $J_{3a,12d} = 8.1$ Hz), 7.17 d.d.d (1H, 6-H, $J_{4,6} = 0.9$, $J_{5,6} = 7.7$, $J_{6,7} = 8.3$ Hz), 7.27 d.t (1H, 5-H, $J_{5,7} = 0.9$, $J_{4,5} = J_{5,6} = 7.7$ Hz), 7.42 br.d (1H, 4-H, $J_{4,5} = 7.7$ Hz), 7.94 br.d (1H, 7-H, $J_{6,7} = 8.3$ Hz). Mass spectrum, m/z (I_{rel} , %): 369 (100) [$M]^+$, 338 (6), 280 (3), 174 (7), 156 (3), 143 (4), 130 (5), 113 (5), 77

(2). Found, %: C 65.13; H 5.08; N 3.99. $C_{20}H_{19}NO_6$. Calculated, %: C 64.99; H 5.21; N 3.76. *M* 369.12.

Methyl (3a*S*^{*},9a*S*^{*},10*R*^{*},11*R*^{*},11a*R*^{*},12a*R*^{*},12b*R*^{*},12c*S*^{*},12d*S*^{*})-11,12b-epoxy-11-methyl-9-oxo-1,2,9,9a,10,11,11a,12a,12c,12d-decahydro-3a*H*-furo[3,2-*c*]oxirano[6,7]isoindolo[2,1-*a*]quinoline-10-carboxylate (XIXb). Yield 58%, colorless crystals, mp 225–227°C (from hexane–ethyl acetate), R_f 0.55 (ethyl acetate). IR spectrum, ν , cm^{−1}: 1740 (COOMe), 1701 (C=O). ¹H NMR spectrum ($CDCl_3$), δ , ppm: 1.55 s (3H, Me), 1.72 m (1H, 1-H), 2.08 m (1H, 1-H), 2.99 d (1H, 10-H, $J_{9a,10}$ = 9.4 Hz), 3.07 d (1H, 9a-H, $J_{9a,10}$ = 9.4 Hz), 3.12 m (1H, 12d-H), 3.32 d (1H, 11a-H, $J_{11a,12a}$ = 3.3 Hz), 3.59 d (1H, 12a-H, $J_{11a,12a}$ = 3.3 Hz), 3.78 s (3H, OMe), 3.78 m (1H, 2-H), 3.92 m (1H, 2-H), 4.50 d (1H, 12c-H, $J_{12c,12d}$ = 2.7 Hz), 5.34 d (1H, 3a-H, $J_{3a,12d}$ = 8.0 Hz), 7.16 d.t (1H, 5-H, $J_{5,7}$ = 1.2, $J_{4,5}$ = $J_{5,6}$ = 7.7 Hz), 7.27 d.d.d (1H, 6-H, $J_{4,6}$ = 1.3, $J_{5,6}$ = 7.7, $J_{6,7}$ = 8.3 Hz), 7.41 d.d (1H, 4-H, $J_{4,6}$ = 1.3, $J_{4,5}$ = 7.7 Hz), 7.92 d.d (1H, 7-H, $J_{5,7}$ = 1.2, $J_{6,7}$ = 8.3 Hz). Mass spectrum, m/z (I_{rel} , %): 383 (100) [M]⁺, 308 (19), 280 (66), 254 (39), 222 (32), 172 (44), 130 (46), 13 (44), 101 (55), 76 (61), 59 (89), 43 (75). Found, %: C 65.67; H 5.39; N 3.82. $C_{21}H_{21}NO_6$. Calculated, %: C 65.79; H 5.52; N 3.65. *M* 383.14.

Methyl (3a*S*^{*},9a*S*^{*},10*R*^{*},11*R*^{*},11a*R*^{*},12a*R*^{*},12b*R*^{*},12c*S*^{*},12d*S*^{*})-11,12b-epoxy-10-methyl-9-oxo-1,2,9,9a,10,11,11a,12a,12c,12d-decahydro-3a*H*-furo[3,2-*c*]oxirano[6,7]isoindolo[2,1-*a*]quinoline-10-carboxylate (XIXc). Yield 54%, colorless crystals, mp 223°C (from hexane–ethyl acetate), R_f 0.25 (hexane–ethyl acetate, 1:2). IR spectrum, ν , cm^{−1}: 1724 (COOMe), 1690 (C=O). ¹H NMR spectrum ($CDCl_3$), δ , ppm: 1.47 s (3H, Me), 1.67 m (1H, 1-H), 2.06 m (1H, 1-H), 2.54 s (1H, 9a-H), 3.09 m (1H, 12d-H), 3.56 d (1H, 11a-H, $J_{11a,12a}$ = 3.3 Hz), 3.58 d (1H, 12a-H, $J_{11a,12a}$ = 3.3 Hz), 3.74 s (3H, OMe), 3.74 m (1H, 2-H), 3.87 m (1H, 2-H), 4.41 d (1H, 12c-H, $J_{12c,12d}$ = 2.8 Hz), 4.52 s (1H, 11-H), 5.30 d (1H, 3a-H, $J_{3a,12d}$ = 7.7 Hz), 7.13 d.t (1H, 5-H, $J_{5,7}$ = 1.5, $J_{4,5}$ = $J_{5,6}$ = 7.7 Hz), 7.24 d.d.d (1H, 6-H, $J_{4,6}$ = 1.7, $J_{5,6}$ = 7.7, $J_{6,7}$ = 8.2 Hz), 7.37 d.d (1H, 4-H, $J_{4,6}$ = 1.7, $J_{4,5}$ = 7.7 Hz), 7.87 d.d (1H, 7-H, $J_{5,7}$ = 1.5, $J_{6,7}$ = 8.2 Hz). Found, %: C 65.55; H 5.33; N 3.81. $C_{21}H_{21}NO_6$. Calculated, %: C 65.79; H 5.52; N 3.65.

Methyl (4a*S*^{*},10a*S*^{*},11*R*^{*},12*R*^{*},12a*R*^{*},13a*R*^{*},13b*R*^{*},13c*S*^{*},13d*S*^{*})-12,13b-epoxy-10-oxo-2,3,10-,10a,11,12,12a,13a,13c,13d-decahydro-1*H*,4*aH*-pyrano[3,2-*c*]oxirano[6,7]isoindolo[2,1-*a*]quinoline-11-carboxylate (XX).** Yield 87%, colorless crystals,

mp 278–280°C (from hexane–ethyl acetate), R_f 0.65 (hexane–ethyl acetate, 1:4). IR spectrum, ν , cm^{−1}: 1691 (C=O), 1734 (COOMe). ¹H NMR spectrum ($CDCl_3$), δ , ppm: 1.44 m (1H, 1-H), 1.55 m (1H, 1-H), 1.67 m (1H, 2-H), 1.82 m (1H, 2-H), 2.63 m (1H, 13d-H), 3.01 d (1H, 11-H, $J_{10a,11}$ = 9.4 Hz), 3.05 d (1H, 10a-H, $J_{10a,11}$ = 9.4 Hz), 3.28 m (1H, 3-H), 3.46 d (1H, 12a-H, $J_{11a,12a}$ = 3.2 Hz), 3.60 d (1H, 13a-H, $J_{12a,13a}$ = 3.2 Hz), 3.63 m (1H, 3-H), 3.78 s (3H, OCH₃), 4.33 d (1H, 13c-H, $J_{13c,13d}$ = 1.9 Hz), 4.76 s (1H, 12-H), 5.13 d (1H, 4a-H, $J_{4a,13d}$ = 5.9 Hz), 7.18 d.t (1H, 6-H, $J_{5,6}$ = $J_{6,7}$ = 7.7, $J_{6,8}$ = 1.0 Hz), 7.28 d.d.d (1H, 7-H, $J_{7,8}$ = 8.2, $J_{6,7}$ = 7.7, $J_{5,7}$ = 0.8 Hz), 7.54 br.d (1H, 5-H, $J_{5,6}$ = 7.7 Hz), 8.06 d.d (1H, 8-H, $J_{7,8}$ = 8.2, $J_{6,8}$ = 1.0 Hz). Mass spectrum, m/z (I_{rel} , %): 383 (93) [M]⁺, 324 (11), 294 (11), 280 (14), 254 (17), 238 (17), 224 (16), 210 (19), 196 (63), 186 (64), 170 (46), 156 (65), 144 (47), 130 (64), 113 (41), 101 (86), 91 (48), 80 (87), 71 (78), 59 (100), 43 (57). Found, %: C 65.97; H 5.67; N 3.44. $C_{21}H_{21}NO_6$. Calculated, %: C 65.79; H 5.52; N 3.65. *M* 383.39.

(3a*S*^{*},9a*S*^{*},10*R*^{*},11*R*^{*},11a*R*^{*},12a*R*^{*},12b*R*^{*},12c*S*^{*},12d*S*^{*})-11,12b-Epoxy-10-phenyl-1,2,10,11-,11a,12a,12c,12d-octahydro-3a*H*-furo[3,2-*c*]oxirano-[6,7]isoindolo[2,1-*a*]quinolin-9(9a*H*)-one (XXIa). Yield 57%, colorless crystals, mp 200°C (from hexane–ethyl acetate), R_f 0.73 (hexane–ethyl acetate, 1:1). IR spectrum: ν 1702 cm^{−1} (C=O). ¹H NMR spectrum ($CDCl_3$), δ , ppm: 1.92 m (1H, 1-H), 2.23 m (1H, 1-H), 2.95 m (1H, 12d-H), 3.11 d (1H, 9a-H, $J_{9a,10}$ = 5.0 Hz), 3.39 d (1H, 11a-H, $J_{11a,12a}$ = 3.3 Hz), 3.55 d (1H, 12a-H, $J_{11a,12a}$ = 3.3 Hz), 3.68 m (1H, 2-H), 3.86 m (1H, 2-H), 3.97 t (1H, 10-H, $J_{9a,10}$ = $J_{10,11}$ = 5.0 Hz), 4.69 d (1H, 12c-H, $J_{12c,12d}$ = 2.8 Hz), 4.84 d (1H, 11-H, $J_{10,11}$ = 5.0 Hz), 5.23 d (1H, 3a-H, $J_{3a,12d}$ = 7.2 Hz), 7.11 br.t (1H, 5-H, $J_{4,5}$ = $J_{5,6}$ = 7.7 Hz), 7.25–7.35 m (6H, H_{arom}), 7.49 d (1H, 4-H, $J_{4,5}$ = 7.7 Hz), 8.60 d (1H, 7-H, $J_{6,7}$ = 8.8 Hz). Found, %: C 74.15; H 5.68; N 3.82. $C_{24}H_{21}NO_4$. Calculated, %: C 74.40; H 5.46; N 3.62. *M* 387.15.

(3a*S*^{*},9a*S*^{*},11*R*^{*},11a*R*^{*},12a*R*^{*},12b*R*^{*},12c*S*^{*},12d*S*^{*})-11,12b-Epoxy-9a-methyl-1,2,10,11,11a,12a-,12c,12d-octahydro-3a*H*-furo[3,2-*c*]oxirano[6,7]isoindolo[2,1-*a*]quinolin-9(9a*H*)-one (XXIb). Yield 48%, colorless crystals, mp 190°C (from hexane–ethyl acetate), R_f 0.33 (hexane–ethyl acetate, 1:1). IR spectrum: ν 1697 cm^{−1} (C=O). ¹H NMR spectrum ($CDCl_3$), δ , ppm: 1.32 s (3H, Me), 1.42 d (1H, *endo*-10-H, ²*J* = 12.7 Hz), 1.88 m (1H, 1-H), 2.16 m (1H, 1-H), 2.49 d.d (1H, *exo*-10-H, ²*J* = 12.7, $J_{exo-10,11}$ = 5.3 Hz), 2.94 m (1H, 12d-H), 3.47 d (1H, 11a-H, $J_{11a,12a}$ =

3.3 Hz), 3.52 d (1H, 12a-H, $J_{11a,12a} = 3.3$ Hz), 3.66 m (1H, 2-H), 3.85 m (1H, 2-H), 4.53 d (1H, 11-H, $J_{exo-10,11} = 5.3$ Hz), 4.58 d (1H, 12c-H, $J_{12c,12d} = 2.8$ Hz), 5.24 d (1H, 3a-H, $J_{3a,12d} = 7.1$ Hz), 7.11 d.t (1H, 5-H, $J_{5,7} = 1.1$, $J_{4,5} = J_{5,6} = 7.6$ Hz), 7.24 m (1H, 6-H), 7.48 br.d (1H, 4-H, $J_{4,5} = 7.6$ Hz), 8.59 d.d (1H, 7-H, $J_{5,7} = 1.1$, $J_{6,7} = 8.5$ Hz). Mass spectrum, m/z (I_{rel} , %): 325 (97) [$M]^+$, 309 (8), 280 (100), 240 (12), 200 (12), 156 (25), 139 (34), 128 (36), 101 (52), 83 (27), 69 (37), 55 (54), 43 (62). Found, %: C 70.37; H 6.02; N 4.17. $C_{19}H_{19}NO_4$. Calculated, %: C 70.14; H 5.89; N 4.31. M 325.13.

(1aS*,2S*,3aR*,10S*,11aS*,11bS*,11cS*)-2,11b-Epoxy-10-ethoxy-1a,3,3a,11,11a,11c-hexahydro-10H-oxirano[6,7]isoindolo[2,1-a]quinolin-4(2H)-one (XXIIa). Yield 48%, colorless crystals, mp 149–150°C (from hexane–ethyl acetate), R_f 0.29 (hexane–ethyl acetate, 1 : 1). IR spectrum: ν 1691 cm⁻¹ (C=O). ¹H NMR spectrum ($CDCl_3$), δ , ppm: 1.27 t (3H, CH_2CH_3 , $^3J = 7.0$ Hz), 1.86 d.d (1H, *endo*-3-H, $J_{3a,endo-3} = 9.1$, $^2J = 12.7$ Hz), 2.10 br.q (1H, 11-H_{ax}, $J_{10,11-ax} = 11.0$, $J_{11a,11-ax} = 12.1$, $^2J = 12.7$ Hz), 2.25 d.d.d (1H, *exo*-3-H, $J_{2,exo-3} = 5.1$, $J_{3a,exo-3} = 3.8$, $^2J = 12.7$ Hz), 2.54 d.d.d (1H, 11-H_{eq}, $J_{10,11-eq} = 5.7$, $J_{11a,11-eq} = 1.5$, $^2J = 12.7$ Hz), 2.80 d.d (1H, 3a-H, $J_{3a,exo-3} = 3.8$, $J_{3a,endo-3} = 9.1$ Hz), 3.43 d (1H, 11c-H, $J_{1a,11c} = 3.2$ Hz), 3.47 d (1H, 1a-H, $J_{1a,11c} = 3.2$ Hz), 3.72 m and 3.57 m (1H each, OCH_2 , $^3J = 7.0$ Hz), 4.40 d.d (1H, 11a-H, $J_{11a,11-ax} = 12.1$, $J_{11a,11-eq} = 1.5$ Hz), 4.62 d (1H, 2-H, $J_{2,exo-3} = 5.1$ Hz), 4.72 d.d (1H, 10-H, $J_{10,11-ax} = 11.0$, $J_{10,11-eq} = 5.7$ Hz), 7.09 br.t (1H, 8-H, $J_{7,8} = J_{8,9} = 7.6$ Hz), 7.23 d.d (1H, 7-H, $J_{6,7} = 8.3$, $J_{7,8} = 7.6$ Hz), 7.55 d (1H, 9-H, $J_{8,9} = 7.6$ Hz), 8.61 d (1H, 6-H, $J_{6,7} = 8.3$ Hz). Mass spectrum, m/z (I_{rel} , %): 313 (100) [$M]^+$, 284 (22), 268 (46), 266 (15), 196 (12), 180 (13), 130 (30), 77 (11). Found, %: C 68.77; H 6.07; N 4.32. $C_{18}H_{19}NO_4$. Calculated, %: C 68.99; H 6.11; N 4.47. M 313.35.

Methyl (1aS*,2S*,3S*,3aR*,10S*,11aS*,11bS*,11cS*)-2,11b-epoxy-10-ethoxy-4-oxo-1a,2,3,3a,4,11,11a,11c-octahydro-10H-oxirano[6,7]isoindolo[2,1-a]quinoline-3-carboxylate (XXIIb). Yield 49%, colorless crystals, mp 189–190°C (from hexane–ethyl acetate), R_f 0.61 (ethyl acetate). IR spectrum, ν , cm⁻¹: 1736 (COOMe), 1701 (C⁴=O). ¹H NMR spectrum ($CDCl_3$) δ , ppm: 1.31 t (3H, CH_2CH_3 , $^3J = 6.9$ Hz), 2.26 br.q (1H, 11-H_{ax}, $J_{10,11-ax} = 11.2$, $J_{11a,11-ax} = 12.5$, $^2J = 12.8$ Hz), 2.56 d.d.d (1H, 11-H_{eq}, $J_{10,11-eq} = 5.9$, $J_{11a,11-eq} = 2.3$, $^2J = 12.8$ Hz), 2.99 d (1H, 3a-H, $J_{3a,3} = 9.5$ Hz), 3.22 d (1H, 3-H, $J_{3a,3} = 9.5$ Hz), 3.47 d (1H, 11c-H, $J_{1a,11c} = 3.3$ Hz), 3.55 d (1H, 1a-H, $J_{1a,11c} =$

3.3 Hz), 3.74 m and 3.59 m (1H each, OCH_2 , $^3J = 6.9$ Hz), 3.77 s (3H, OMe), 4.41 d.d (1H, 11a-H, $J_{11a,11-ax} = 12.5$, $J_{11a,11-eq} = 2.3$ Hz), 4.78 d.d (1H, 10-H, $J_{10,11-ax} = 11.2$, $J_{10,11-eq} = 5.9$ Hz), 4.84 s (1H, 2-H), 7.13 t (1H, 8-H, $J_{7,8} = J_{8,9} = 7.7$ Hz), 7.25 d.d (1H, 7-H, $J_{6,7} = 8.2$, $J_{7,8} = 7.7$ Hz), 7.58 d (1H, 9-H, $J_{8,9} = 7.7$ Hz), 8.56 d (1H, 6-H, $J_{6,7} = 8.2$ Hz). Mass spectrum, m/z (I_{rel} , %): 371 (81) [$M]^+$, 326 (17), 295 (32), 267 (26), 238 (52), 196 (46), 182 (24), 167 (21), 130 (39), 113 (24), 101 (36), 76 (100), 55 (87), 43 (77). Found, %: C 64.87; H 5.17; N 3.32. $C_{20}H_{21}NO_6$. Calculated, %: C 64.68; H 5.70; N 3.77. M 371.38.

Aromatization of carboxylic acids Va and VI (general procedure). A solution of ~1 g (~2.8 mmol) of carboxylic acid **Va** or **VI** in 15 ml of phosphoric acid was stirred for 30 min at 85°C. The mixture was cooled to 20°C and poured into 50 ml of water, and the precipitate was filtered off and recrystallized from propan-2-ol–DMF.

(3aS*,13bS*,13cS*)-9-Oxo-1,2,3a,9,13b,13c-hexahydrofuro[3,2-c]isoindolo[2,1-a]quinoline-10-carboxylic acid (XXIIIa). Yield 89%, colorless crystals, mp 236–238°C (*i*-PrOH–DMF). IR spectrum, ν , cm⁻¹: 1705 (COOH), 1620 (C⁹=O). ¹H NMR spectrum ($DMSO-d_6$), δ , ppm: 0.99 d.d.d.d (1H, 1-H, $^2J = 12.2$, $J_{2,1} = 9.4$, $J_{2,1} = 7.4$, $J_{1,13c} = 10.2$ Hz), 1.45 d.d.d (1H, 1-H, $^2J_{1,1} = 12.2$, $J_{2,1} = 7.2$, $J_{1,2} = 3.9$ Hz), 3.51 br.d.t (1H, 2-H, $^2J = 8.6$, $J_{2,1} = 3.9$, $J_{2,1} = 7.4$ Hz), 3.58 d.d.d.d (1H, 13c-H, $J_{13c,13b} = 8.0$, $J_{13c,3a} = 3.8$, $J_{13c,1} = 8.7$, $J_{13c,1} = 10.2$ Hz), 3.66 br.q (1H, 1-H, $^2J = 8.6$, $J_{2,1} = 7.2$, $J_{2,1} = 9.4$ Hz), 5.35 d (1H, 13b-H, $J_{13b,13c} = 8.0$ Hz), 5.50 d (1H, 3a-H, $J_{3a,13c} = 3.8$ Hz), 7.28 d.t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.5$, $J_{5,7} = 1.0$ Hz), 7.42 d.t (1H, 6-H, $J_{6,5} = J_{6,7} = 7.7$, $J_{4,6} = 1.3$ Hz), 7.50 d.d (1H, 4-H, $J_{4,5} = 7.5$, $J_{4,6} = 1.3$ Hz), 7.88 t (1H, 12-H, $J_{11,12} = J_{12,13} = 7.5$ Hz), 8.01 d (1H, 13-H, $J_{12,13} = 7.5$ Hz), 8.06 d (1H, 11-H, $J_{11,12} = 7.5$ Hz), 8.22 d.d (1H, 7-H, $J_{6,7} = 7.7$, $J_{5,7} = 1.0$ Hz). Mass spectrum, m/z (I_{rel} , %): 321 (70) [$M]^+$, 277 (100), 247 (14), 232 (22), 204 (15), 178 (5), 115 (13), 89 (6), 77 (12), 63 (6), 39 (10). Found, %: C 70.93; H 4.52; N 4.71. $C_{19}H_{15}NO_4$. Calculated, %: C 71.02; H 4.71; N 4.36. M 321.33.

(4aS*,14bS*,14cS*)-10-Oxo-2,3,4a,10,14b,14c-Hexahydro-1H-isoindolo[2,1-a]pyrano[3,2-c]quinoline-11-carboxylic acid (XXIIIc). Yield 77%, colorless crystals, mp 260°C (*i*-PrOH–DMF). IR spectrum, ν , cm⁻¹: 1706 (COOH), 1623 (C¹⁰=O). ¹H NMR spectrum ($DMSO-d_6$), δ , ppm: 0.63 d.q (1H, 1-H, $J_{1,2} = 3.7$, $J_{1,3} = 12.5$ Hz), 0.83 m (1H, 1-H), 1.33 m (1H, 2-H), 1.53 m (1H, 2-H), 3.01 m (1H, 14c-H), 3.08 m (1H,

3-H), 3.57 d.d (1H, 3-H, $J_{2,3} = 4.5$, $J_{1,3} = 12.5$ Hz), 5.31 d.d (1H, 14b-H, $J_{14a,14b} = 0.7$, $J_{14b,14c} = 5.6$ Hz), 5.38 d (1H, 4a-H, $J_{4a,5} = 2.8$ Hz), 7.32 d.t (1H, 6-H, $J_{5,6} = 1.1$, $J_{6,7} = 7.6$ Hz), 7.43 d.d.d (1H, 7-H, $J_{7,8} = 0.8$, $J_{6,7} = 7.6$, $J_{5,7} = 8.1$ Hz), 7.58 d.d (1H, 5-H, $J_{5,6} = 1.1$, $J_{5,7} = 7.7$ Hz), 7.88 br.t (1H, 13-H, $J_{12,13} = 7.8$, $J_{13,14} = 7.6$ Hz), 7.99 d.d (1H, 14-H, $J_{13,14} = 7.6$, $J_{14,14a} = 0.8$ Hz), 8.04 br.d (1H, 12-H, $J_{12,13} = 7.8$ Hz), 8.41 d.d (1H, 8-H, $J_{7,8} = 1.0$, $J_{6,8} = 8.3$ Hz). Mass spectrum, m/z (I_{rel} , %): 335 (20) [$M]^+$, 291 (44), 232 (31), 204 (53), 127 (29), 115 (37), 102 (48), 88 (32), 77 (100), 63 (54), 55 (27), 51 (72), 39 (69). Found, %: C 71.52; H 5.36; N 4.33. $C_{20}H_{17}NO_4$. Calculated, %: C 71.63; H 5.11; N 4.18. M 335.35.

(3aS*,13bS*,13cS*)-1,2,13b,13c-Tetrahydrofuro[3,2-*c*]isoindolo[2,1-*a*]quinolin-9(3aH)-one (XXIIIb).

A solution of 1 g (3.39 mmol) of compound **VIIIa** in 15 ml of phosphoric acid was stirred for 1 h at 85°C. The mixture was cooled, poured into 50 ml of water, and extracted with ethyl acetate (3×50 ml). The extract was dried over anhydrous magnesium sulfate, the solvent was distilled off, and the residue was recrystallized from hexane–ethyl acetate. Yield 0.33 g (35%), colorless crystals, mp 118–120°C (from hexane–ethyl acetate), R_f 0.65 (hexane–ethyl acetate, 1:1). IR spectrum: ν 1699 cm⁻¹ (C=O). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.27 d.t (1H, 1-H, $^2J = 12.4$, $J_{1,13c} = J_{1,2} = 9.0$ Hz), 1.57 d.d.t (1H, 1-H, $J_{1,2} = 4.5$, $J_{1,2} = J_{1,13c} = 7.9$, $^2J = 12.4$ Hz), 3.38 d.q (1H, 13c-H, $J_{13b,13c} = 3.4$, $J = 9.3$ Hz), 3.67 d.t (1H, 2-H, $J_{1,2} = 4.5$, $J = 8.7$ Hz), 3.80 br.q (1H, 2-H, $^2J = J_{1,2} = 7.9$ Hz), 5.14 d (1H, 13b-H, $J_{13b,13c} = 3.4$ Hz), 5.41 d (1H, 3a-H, $J_{3a,13c} = 7.9$ Hz), 7.22 t (1H, 5-H, $J_{4,5} = J_{5,6} = 7.5$ Hz), 7.40 d.d (1H, 6-H, $J_{6,7} = 8.2$, $J_{5,6} = 7.5$ Hz), 7.54 d (2H, 4-H, 13-H, $J_{4,5} = 7.5$, $J_{12,13} = 7.5$ Hz), 7.56 t (1H, 11-H, $J_{10,11} = J_{11,12} = 7.5$ Hz), 7.65 t (1H, 12-H, $J_{11,12} = J_{12,13} = 7.5$ Hz), 7.98 d (1H, 10-H, $J_{10,11} = 7.5$ Hz), 8.43 d (1H, 7-H, $J_{6,7} = 8.2$ Hz). Mass spectrum, m/z (I_{rel} , %): 277 (91) [$M]^+$, 248 (86), 232 (100), 218 (59), 204 (42), 165 (22), 128 (32), 115 (97), 105 (41), 89 (78), 76 (76), 59 (74), 51 (36), 43 (49). Found, %: C 78.11; H 5.23; N 5.37. $C_{18}H_{15}NO_2$. Calculated, %: C 77.96; H 5.45; N 5.05. M 277.32.

(3aS*,13bS*,13cS*)-5-Nitro-9-oxo-1,2,3a,9,13b-,13c-hexahydrofuro[3,2-*c*]isoindolo[2,1-*a*]quinoline-10-carboxylic acid (XXIVa). Compound **XXIIIa**, 0.49 g (1.53 mmol), was dissolved in 9 ml of concentrated sulfuric acid, 0.18 g (1.8 mmol) of potassium nitrate was added in portions under stirring, and the mixture was stirred for 90 min at 45–50°C, cooled, and poured into 40 ml of water. The precipitate was filtered

off, washed with water until neutral washings, dried in air, and recrystallized from *i*-PrOH–DMF. Yield 0.32 g (57%), light yellow crystals, mp 282–284°C. IR spectrum, ν , cm⁻¹: 1720 (COOH), 1631 (C=O). ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 1.02 m (1H, 1-H), 1.50 m (1H, 1-H), 3.55 m (1H, 2-H), 3.62 m (1H, 13c-H), 3.72 m (1H, 2-H), 5.45 d (1H, 13b-H, $J_{13b,13c} = 8.1$ Hz), 5.54 d (1H, 3a-H, $J_{3a,13c} = 3.4$ Hz), 7.87 m (2H, 11-H, 13-H), 7.66 m (1H, 12-H), 8.27 d.d (1H, 6-H, $J_{4,6} = 2.8$, $J_{6,7} = 9.0$ Hz), 8.30 d (1H, 4-H, $J_{4,6} = 2.8$ Hz), 8.52 d (1H, 7-H, $J_{6,7} = 9.0$ Hz). Mass spectrum, m/z (I_{rel} , %): 366 (18) [$M]^+$, 322 (100), 304 (21), 277 (17), 231 (11), 217 (15), 189 (10), 151 (6), 115 (9), 89 (6), 75 (5), 63 (5). Found, %: C 62.05; H 3.61; N 7.86. $C_{19}H_{14}N_2O_6$. Calculated, %: C 62.30; H 3.85; N 7.65. M 366.32.

(3aS*,13bS*,13cS*)-5-Nitro-1,2,13b,13c-tetrahydrofuro[3,2-*c*]isoindolo[2,1-*a*]quinolin-9(3aH)-one (XXIVb). A solution of 0.50 g (1.8 mmol) of compound **XXIIIb** in 8 ml of concentrated sulfuric acid was cooled with ice, 0.18 g (1.82 mmol) of potassium nitrate was added in portions under stirring, and the mixture was stirred for 1 h at –5 to 0°C, and poured into 50 ml of water. The precipitate was filtered off, washed with water and a solution of sodium carbonate, dried in air, and recrystallized from *i*-PrOH–DMF. Yield 0.22 g (38%), yellow crystals, mp 210–212°C. IR spectrum: ν 1710 cm⁻¹ (C=O). ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 0.96 m (1H, 1-H), 1.47 m (1H, 1-H), 3.55 m (2H, 2-H, 13c-H), 3.71 q (1H, 2-H, $J = 7.8$ Hz), 5.43 d (1H, 13b-H, $J_{13b,13c} = 7.7$ Hz), 5.47 d (1H, 3a-H, $J_{3a,13c} = 3.2$ Hz), 7.61 br.t (1H, 11-H, $J_{10,11} = J_{11,12} = 7.6$ Hz), 7.77 br.t (1H, 12-H, $J_{11,12} = J_{12,13} = 7.6$ Hz), 7.80 br.d (1H, 13-H, $J_{12,13} = 7.6$ Hz), 7.87 d (1H, 10-H, $J_{10,11} = 7.6$ Hz), 8.26 d.d (1H, 6-H, $J_{4,6} = 2.4$, $J_{6,7} = 8.6$ Hz), 8.27 d (1H, 4-H, $J_{4,6} = 2.4$ Hz), 8.56 br.d (1H, 7-H, $J_{6,7} = 8.6$ Hz). Mass spectrum, m/z (I_{rel} , %): 322 (100) [$M]^+$, 306 (7), 292 (36), 277 (21), 265 (6), 247 (8), 231 (8), 218 (10), 205 (4), 76 (14), 59 (19), 43 (18). Found, %: C 66.88; H 4.51; N 8.86. $C_{18}H_{14}N_2O_4$. Calculated, %: C 67.07; H 4.38; N 8.69. M 322.31.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 07-03-00083a).

REFERENCES

- Zubkov, F.I., Zaitsev, V.P., Peregudov, A.S., Mikhailova, N.M., and Varlamov, A.V., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2007, p. 1023.

2. Zubkov, F.I., Zaitsev, V.P., Nikitina, E.V., Mikhailova, N.M., Aleksandrov, G.G., Borisov, R.S., and Varlamov, A.V., *Khim. Geterotsikl. Soedin.*, 2005, p. 2.
3. Kouznetsov, V.V., Cruz, U.M., Zubkov, F.I., and Nikitina, E.V., *Synthesis*, 2007, p. 375.
4. Povarov, A.S., Grigos, V.I., and Mikhailov, B.M., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1963, p. 2039.
5. Kouznetsov, V.V., *Tetrahedron*, 2009, vol. 65, p. 2721.
6. Zubkov, F.I., Nikitina, E.V., Turchin, K.F., Aleksandrov, G.G., Safronova, A.A., Borisov, R.S., and Varlamov, A.V., *J. Org. Chem.*, 2004, vol. 69, p. 432.
7. Sader-Bakaouni, L., Charton, O., Kunesch, N., and Tillequin, F., *Tetrahedron*, 1998, vol. 54, p. 1773.
8. Nelson, W.L. and Allen, D.R., *J. Heterocycl. Chem.*, 1972, vol. 9, p. 561.
9. Varlamov, A.V., Boltukhina, E.V., Zubkov, F.I., Sidorenko, N.V., Chernyshev, A.I., and Grudinin, D.G., *Khim. Geterotsikl. Soedin.*, 2004, p. 27.
10. Zubkov, F.I., Boltukhina, E.V., Turchin, K.F., Borisov, R.S., and Varlamov, A.V., *Tetrahedron*, 2005, vol. 61, p. 4099.