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Synthesis of 7-Hydroxy-6-alkoxy Derivatives of 3,4-Dihydroisoquinoline by Ritter Reaction

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Abstract—1-Substituted 6,7-dialkoxy-3,4-dihydroisoquinolines containing in the position *7* of the isoquinoline ring propoxy- or butoxy groups in the course of maintaining in the concentrated sulfuric acid are converted into 1-substituted 6-alkoxy-7-hydroxy-3,4-dihydroisoquinolines.

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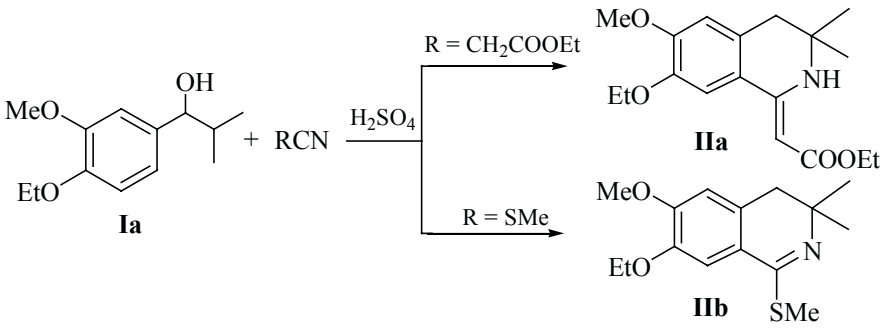
The simplest synthesis of 1-substituted derivaties of 7-hydroxy-6-methoxy-3,3-dimethyl-3,4-dihydroisoquinoline, analogs of natural alkaloids, consists in the reaction of 1-(4-benzyloxy-3-methoxyphenyl)-2-methyl-1-propanol with nitriles in concentrated sulfuric acid [1] where the cyclization proceeds simultaneously with the removal of the benzyl protection, and this is rather unusual. The removal of the alkoxy group occurs as a rule at heating the corresponding aromatic-aliphatic ethers in hydrohalogenic acid [2–7]. The goal of this research is the investigation of the effect of the substituents in the position *4* of 1-(4-alkoxy-3-methoxyphenyl)-2-methyl-1-propanol on the character of compounds formed in the course of Ritter heterocyclization. Carbinols and styrenes used in the study were obtained from the corresponding derivatives of vanillin or isovanillin and isopropylmagnesium bromide in THF [8].

In the reaction of 1-(3-methoxy-4-ethoxyphenyl)-2-methylpropan-1-ol (**Ia**) with nitriles 1-substituted 3,3-dimethyl-6-methoxy-7-ethoxy-3,4-dihydroisoquinolines **IIa, IIb** were obtained (Scheme 1).

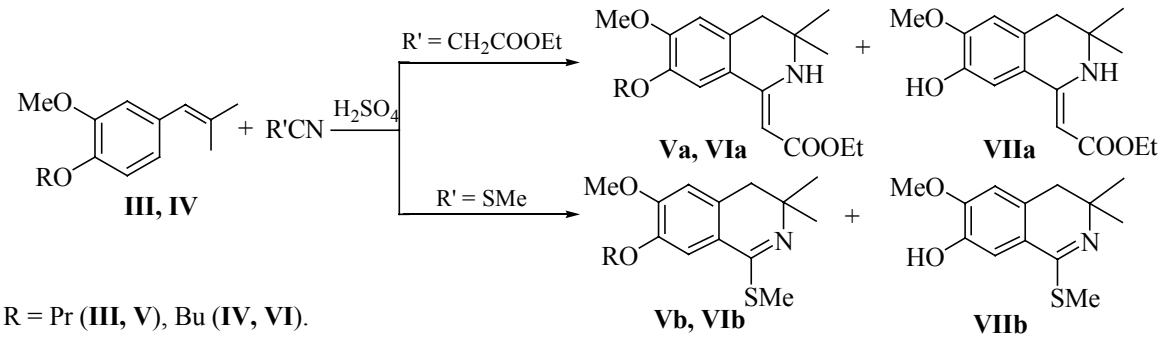
The subsequent increasing the length of the substituent in the position *4* of styrenes **III, IV** led to the formation of a mixture of 6-methoxy-7-alkoxy-substituted **Va, Vb, VIa, VIb** and 3,3-dialkyl-6-methoxy-7-hydroxy-3,4-dihydroisoquinolines **VIIa, VIIb** (Scheme 2). Characteristics of compounds **VIIa, VIIb** were given in [1].

The reactions of alcohols **VIII, IX** having propoxy or butoxy substituents in the position *3* and a methoxy group in the position *4* furnished only 6,7-dialkoxy derivatives **Xa, Xb, XIa, XIb**. The absence of 3,4-dihydroisoquinolines having an OH group was proved by the GC-MS investigation of the reaction mixture. The reaction of isobutyric aldehyde with 1,2-diethoxybenzene and nitriles (ethyl

Scheme 1.



Scheme 2.



R = Pr (**III, V**), Bu (**IV, VI**).

R[1] = Et (**XIIa, XIIb**), Pr (**VIII, X**), Bu (**IX, XI**); R[2] = Me (**VIII, Xa, Xb, XIa, XIb**), Et (**XIIa, XIIb**).

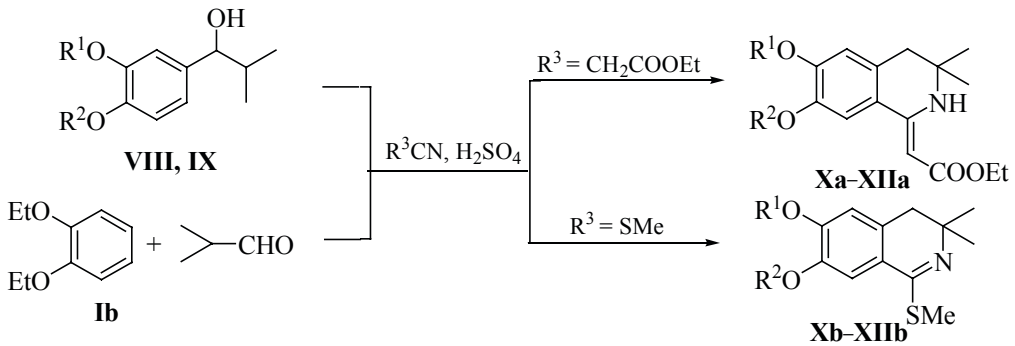
cyanoacetate, methyl thiocyanate) resulted in corresponding derivatives of 3,4-dihydroisoquinoline **XIIa, XIIb** (Scheme 3) [9].

The reaction with *o*-dipropoxy- or *o*-dibutoxybenzene, with α-branched aldehydes and nitrile within the minimal possible time (~2 min) afforded the corresponding 6,7-dialkoxy-3,4-dihydroisoquinolines **XIIIa, XIIIb, XIVa, XIVb, XVa** and the reaction with the *o*-dialkoxybenzenes within 20 min gave the corresponding 6,7-dialkoxy-substituted compounds **XIIIa, XIIIb, XIVa, XIVb, XVa** and 3,3-dialkyl-6-alkoxy-7-hydroxy-3,4-dihydroisoquinolines **XVIa, XVIIa, XVIIb, XVIIIa** (Scheme 4) which were isolated by the fractional crystallization.

The structure of compounds obtained was confirmed by ^{1}H and ^{13}C NMR, IR, and mass spectra. In the ^{1}H NMR spectra of compounds **XVIa, XVIIa, XVIIb, XVIIIa** a singlet is observed in the region 5.47–5.82 ppm, and in the IR spectrum an absorption band is present in the region 3300–3340 cm^{-1} (OH). The position of the hydroxy group in ethyl [6-butoxy-7-hydroxy-3,3-dimethyl-3,4-dihydroisoquinolin-1(2*H*)-ylidene]ethanoate (**XVIIa**) was established with the help of the 2D spectrum. The position of the butoxy group at the atom C*^{6}* is indicated by the presence in the HMBC spectrum of the cross-peak C*^{6}*/H$^{OC\underline{H}_2-C_3H_7}$ (148.1/4.04 ppm). In the 2D NMR spectrum ^{13}C–^{1}H (HMBC) also appeared cross-peaks corresponding to the assumed structure: C*^{1}*/H*^{8}* (155.3/7.22 ppm), C*^{6}*/H*^{8}* (148.1/7.22 ppm), C*^{7}*/H*^{5}* (144.2/6.57 ppm), C*^{4a}*/H*^{8}* (127.8/7.22 ppm), C*^{8a}*/H*^{5}* (121.0/6.57 ppm), C*^{8a}*/H^{NH} (121.0/8.91 ppm), C*^{4}*/H*^{5}* (41.6/6.57 ppm). At keeping compounds **XIIIa, XIVa, XIVb, XVa** in concn. sulfuric acid for 2 h at room temperature compounds **XVIa, XVIIa, XVIIb, XVIIIa** formed in 49–71% yields.

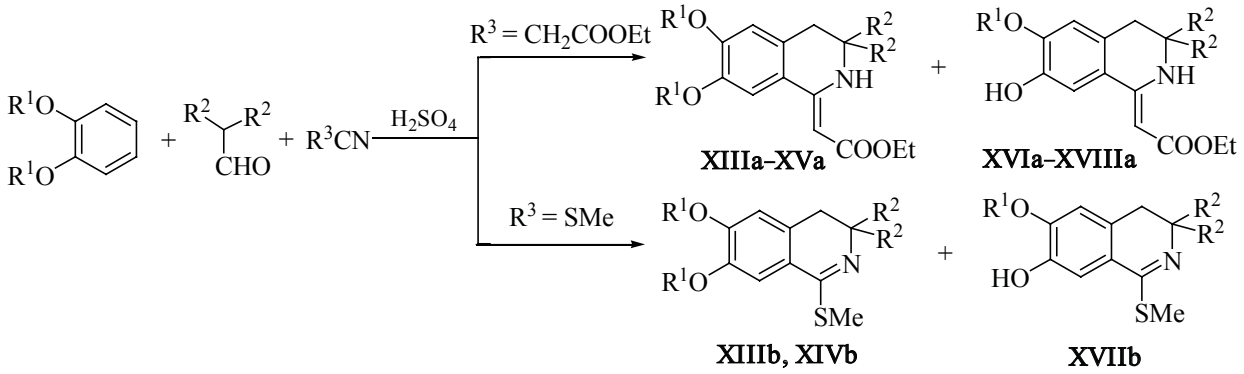
Evidently the primary formed 6,7-dialkoxy-substituted 3,4-dihydroisoquinoline in the concn. sulfuric acid is protonated at the oxygen atom in the position *7* caus-

Scheme 3.



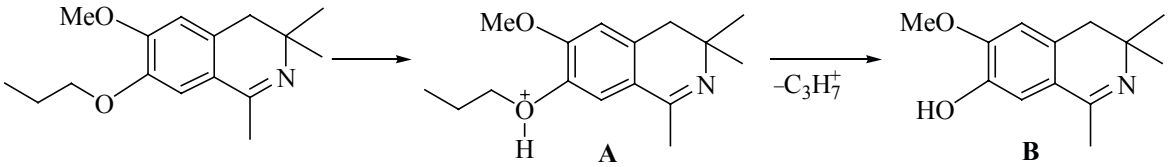
R[1] = Et (**XIIa, XIIb**), Pr (**VIII, X**), Bu (**IX, XI**); R[2] = Me (**VIII, Xa, Xb, XIa, XIb**), Et (**XIIa, XIIb**).

Scheme 4.



R^2 = Me, R^1 = Pr (**XIII, XVI**), Bu (**XIV, XVII**); R^1 = Bu , R^2,R^2 = $(CH_2)_5$ (**XV, XVIII**).

Scheme 5.



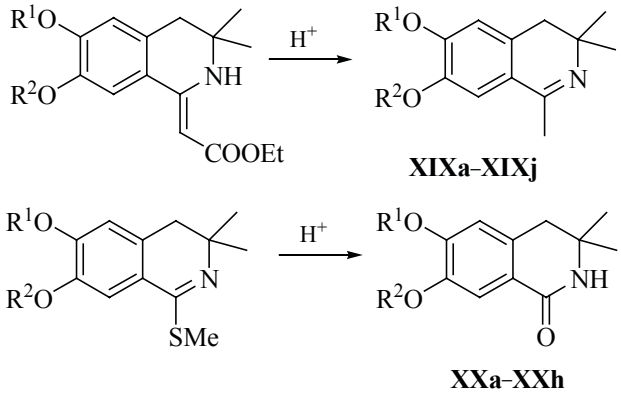
ing the cleavage of a propyl (or butyl) cation and the formation of the 7-hydroxy-3,4-dihydroisoquinoline (Scheme 5).

The calculation performed by the semiempirical method PM3 (HyperChem 7.01) demonstrated that the protonation of oxygen atom in the position *7* is more favorable by energy than the protonation in the position *6*. The difference is 20 kJ mol^{-1}. The transition **A** → **B** is accompanied by the enthalpy decrease by 8 kJ mol^{-1}. Analogous calculations for 6-methoxy-7-ethoxy-substituted 3,4-dihydroisoquinoline showed that the protonation by positions *6* and *7* can occur virtually with equal probability, and the cleavage of ethyl cation is unfavorable by energy (increase in the enthalpy by ~48 kJ mol^{-1}).

The heating of esters of isoquinolylideneacetic acids or thiolactim esters in dilute acids results in 1-methyl derivatives of 3,4-dihydroisoquinoline **XIXa–XIXj** and ketones **XXa–XXh** respectively (Scheme 6) with the conservation of the substituents in the aromatic part of the isoquinoline structure.

Compounds **XIXd, XIXe, XIXh** were isolated in the form of hydrochlorides **XXIa–XXIc** respectively.

Scheme 6.



R^1 = Me, R^2 = Et (**a**), Pr (**b**), Bu (**c**); R^2 = Me, R^1 = Pr (**d**), Bu (**e**); R^1 = R^2 = Et (**f**), Pr (**g**), Bu (**h**); R^2 = OH, R^1 = Pr (**i**), Bu (**j**).

EXPERIMENTAL

Melting points were measured on a PTP device. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Varian Mercury plus 300 in $CDCl_3$ at 300 and 75 MHz respectively, internal reference HMDS. IR spectra were

recorded on a spectrophotometer Specord M80 from mulls in mineral oil. Elemental analysis was carried out on an analyzer CHNS-932 Leco Corporation. The reaction progress was monitored and the purity of compounds obtained was checked by TLC on Sorbfil plates, development with 0.5% solution of chloranil in toluene. Mass spectra were obtained on a GC-MS instrument Agilent 6890N/5975B (EI, 70 eV). At the analysis of compounds **Va, VIa, XIa, XIIIa** the products of their decarboethoxylation were registered formed as a result of the thermolysis of the compounds in the vaporizer, identical to compounds **XIXb**, **XIXc, XIXe, XIXg** respectively. Mass spectra of compounds **IIa, Xa, XIIa, XIVa, XVIa, XVIIa** were registered on a mass spectrometer Finnigan MAT.

1-Substituted 3,4-dihydroisoquinolines V, VI, X, XI. *a*. A mixture of 0.01 mol of an appropriate alcohol or alkenylbenzene and 0.01 mol of nitrile was added dropwise to 5 ml of concn. H_2SO_4 cooled to 5–10°C. The mixture was stirred at 20–25°C for 20 min. The reaction mixture was poured into water and neutralized with sodium carbonate to pH 8. The reaction product was extracted into CH_2Cl_2, the extract was washed with water, dried with anhydrous $MgSO_4$, the solvent was distilled off, the residue was recrystallized.

1-Substituted 3,4-dihydroisoquinolines XIIIa–XVIIIa, XIIIb, XIVb, XVIIb. *b*. A mixture of 0.01 mol of arene, 0.72 g (0.01 mol) of isobutyric aldehyde, and 0.01 mol of nitrile was added dropwise to 5 ml of concn. H_2SO_4 at 5–10°C. Further workup was carried out as in procedure *a*.

1,3,3-Trimethyl-3,4-dihydroisoquinolines XIXa–XIXj. *c*. Compounds **XIXa–XIXj** were obtained by heating the corresponding ethyl 3,4-dihydroisoquinolin-1(2*H*)-ideneacetates in 20% H_2SO_4 within 2.5 h. Further workup was carried out as in procedure *a*.

6,7-Dialkoxy-3,3-dimethyl-3,4-dihydroisoquinolin-1(2*H*)-ones XXa–XXh. *d*. Compounds **IIb, Vb**, **VIb, Xb–XIVb** were heated in 80% CH_3COOH for 2 h in the presence of a catalytic quantity of sodium acetate. Further workup was carried out as in procedure *a*.

Hydrochlorides XXIa–XXIc were obtained by passing gaseous HCl thorough the ethyl acetate solution of compounds **XIXd, XIXe, XIXh** respectively. The separated precipitate was filtered off and recrystallized.

Ethyl [3,3-dimethyl-6-methoxy-7-ethoxy-3,4-dihydroisoquinolin-1(2*H*)-ylidene]ethanoate (IIa). Yield 1.12 g (35%), mp 136–138°C (EtOH). IR spectrum, cm^{-1}: 3250, 1648, 1600, 1570, 1520. ^1H NMR spectrum, δ, ppm: 1.27 s (6H, 2Me), 1.29 m (3H, $OCH_2\underline{Me}$), 1.46 t (3H, Me, *J* 7.1 Hz), 2.74 s (2H, CH_2), 3.89 s (3H, OMe), 4.12 m (4H, $2OC\underline{H}_2Me$), 5.00 s (1H, CH=), 6.60 s ($1H_{arom}$), 7.12 s ($1H_{arom}$), 8.92 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 14.6 (Me), 14.7 (Me), 28.4 ($C^3\underline{C}H_3$), 41.6 (C^4), 49.3 (C^3), 55.8 (OCH_3), 58.3 (OCH_2), 64.5 (OCH_2), 76.4 (CH=), 109.5 (C^8), 111.4 (C^5), 120.6 (C^{8a}), 128.7 (C^{4a}), 146.9 (C^7), 151.5 (C^6), 155.4 (C^1), 171.0 (C=O). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 319 (49), $[M - Me]^+$ 304 (20), $[M - OC_2H_5]^+$ 274 (17), 258 (100), 247 (32), 232 (32). Found, %: C 67.40; H 7.79; N 4.37. $C_{18}H_{25}NO_4$. Calculated, %: C 67.69; H 7.89; N 4.39.

3,3-Dimethyl-1-methylsulfanyl-6-methoxy-7-ethoxy-3,4-dihydroisoquinoline (IIb). Yield 0.84 g (30%), mp 79–80°C (EtOH). IR spectrum, cm^{-1}: 1596, 1566, 1514. ^1H NMR spectrum, δ, ppm: 1.16 s (6H, 2Me), 1.43 t (3H, Me, *J* 6.9 Hz), 2.38 s (3H, SMe), 2.58 s (2H, CH_2), 3.85 s (3H, OMe), 4.08 q (2H, OCH_2), 6.59 s ($1H_{arom}$), 7.14 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 12.2 (Me), 14.8 (SMe), 28.3 ($C^3\underline{C}H_3$), 38.9 (C^4), 55.7 (C^3), 55.9 (OMe), 64.5 (OCH_2), 109.6 (C^8), 111.0 (C^5), 121.3 (C^{8a}), 129.3 (C^{4a}), 146.6 (C^7), 151.3 (C^6), 159.4 (C^1). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 279 (25), $[M - Me]^+$ 264 (100), 250 (14), 162 (10). Found, %: C 64.00; H 7.44; N 5.00; S 11.16. $C_{15}H_{21}NO_2S$. Calculated, %: C 64.48; H 7.58; N 5.01; S 11.48.

2-Methoxy-4-(2-methylprop-1-enyl)-1-propoxybenzene (III). Yield 60%, bp 124–143°C (2 mm Hg). ^1H NMR spectrum, δ, ppm: 1.02 t (3H, Me, *J* 7.5 Hz), 1.81–1.87 m (8H, 2Me + CH_2), 3.84 s (3H, OMe), 3.96 t (2H, OCH_2, *J* 6.8 Hz), 6.19 s (1H, CH), 6.74–6.83 m ($3H_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 220 (96), 179 (12), 178 (100), 163 (32), 147 (12), 131 (38).

1-Butoxy-2-methoxy-4-(2-methylprop-1-enyl)-benzene (IV). Yield 58%, bp 115–135°C (2 mm Hg). ^1H NMR spectrum, δ, ppm: 0.94–1.00 m (3H, Me), 1.44–1.52 m (2H, CH_2), 1.79–1.88 m (8H, 2Me + CH_2), 3.84 s (3H, OMe), 4.00 t (2H, OCH_2, *J* 6.9 Hz), 6.19 s (1H, CH), 6.74–6.84 m ($3H_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 234 (70), 179 (12), 178 (100), 163 (25), 131 (28).

Ethyl [3,3-dimethyl-6-methoxy-7-propoxy-3,4-dihydroisoquinolin-1(2*H*)-ylidene]ethanoate (Va). Yield 1.40 g (42%), mp 134–135°C (EtOH). IR spectrum, cm^{-1}: 3265, 1652, 1598, 1574, 1520. ^1H NMR spectrum, δ, ppm: 1.04 t (3H, Me, *J* 7.5 Hz), 1.27 s (6H, 2Me), 1.29 m (3H, $OCH_2\underline{Me}$), 1.86 m (2H, CH_2), 2.73 s (2H, CH_2), 3.88 s (3H, OMe), 3.96 t (2H, OCH_2, *J* 6.8 Hz),

4.15 q (2H, OC$\underline{H}_2$Me), 5.00 s (1H, CH=), 6.60 s (1H_{arom}), 7.13 s (1H_{arom}), 8.93 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 10.4 (OCH$_2$CH$_2$C$\underline{H}_3$), 14.6 (OCH$_2$C$\underline{H}_3$), 22.4 (OCH$_2$C$\underline{H}_2$Me), 28.4 (C^{3}C$\underline{H}_3$), 41.6 (C^4), 49.3 (C^4), 55.8 (OMe), 58.3 (OC$\underline{H}_2$Me), 70.7 (OC$\underline{H}_2$CH$_2$Me), 76.4 (CH=), 109.7 (C^8), 111.5 (C^5), 120.6 (C^{8a}), 128.6 (C^{4a}), 147.2 (C^7), 151.6 (C^6), 155.5 (C^1), 171.0 (C=O). Found, %: C 68.60; H 7.84; N 4.19. $C_{19}H_{27}NO_4$. Calculated, %: C 68.44; H 8.16; N 4.20.

3,3-Dimethyl-1-methylsulfanyl-6-methoxy-7-propoxy-3,4-dihydroisoquinoline (Vb). Yield 0.79 g (27%), mp 72–74°C (EtOH). IR spectrum, cm^{-1}: 1702, 1600, 1568, 1518. ^{1}H NMR spectrum, δ, ppm: 1.04 t (3H, Me, *J* 7.7 Hz), 1.18 s (6H, 2Me), 1.85 m (2H, CH$_2$), 2.41 s (3H, SMe), 2.60 s (2H, CH$_2$), 3.87 s (3H, OMe), 3.98 t (2H, OCH$_2$, *J* 7.7 Hz), 6.61 s (1H_{arom}), 7.16 s (1H_{arom}). ^{13}C NMR spectrum, δ, ppm: 10.4 (Me), 12.1 (SMe), 22.4 (OCH$_2$C$\underline{H}_2$Me), 28.3 (C^{3}C$\underline{H}_3$), 38.9 (C^4), 55.7 (C^3), 55.9 (OMe), 70.8 (OCH$_2$), 109.9 (C^8), 111.1 (C^5), 121.2 (C^{8a}), 129.2 (C^{4a}), 146.8 (C^7), 151.4 (C^6), 159.4 (C^1). Mass spectrum, *m/z* (I_{rel}, %): [*M*]$^+$ 293 (24), [*M* – Me]$^+$ 278 (100), 250 (15), 236 (11), 162 (11). Found, %: C 65.61; H 7.82; N 4.85; S 10.88. $C_{16}H_{23}NO_2S$. Calculated, %: C 65.49; H 7.90; N 4.77; S 10.93.

Ethyl [7-butoxy-3,3-dimethyl-6-methoxy-3,4-dihydroisoquinolin-1(2*H*)-ylidene]ethanoate (VIa). Yield 1.25 g (36%), mp 92–93°C (EtOH). IR spectrum, cm^{-1}: 1646, 1602, 1576, 1516. ^{1}H NMR spectrum, δ, ppm: 1.12 t (3H, Me), 1.41 s (6H, 2Me), 1.42 t (3H, OCH$_2$C$\underline{H}_3$), 1.63 m (2H, OCH$_2$CH$_2$C$\underline{H}_2$Me), 1.96 m (2H, OCH$_2$C$\underline{H}_2$CH$_2$Me), 2.88 s (2H, CH$_2$), 4.01 s (3H, OMe), 4.14 t (2H, OCH$_2$), 4.29 q (2H, OC$\underline{H}_2$Me), 5.15 s (1H, CH=), 6.73 s (1H_{arom}), 7.27 s (1H_{arom}), 8.92 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 13.7 (OCH$_2$CH$_2$CH$_2$C$\underline{H}_3$), 14.6 (OCH$_2$C$\underline{H}_3$), 19.1 (OCH$_2$CH$_2$C$\underline{H}_2$Me), 28.4 (C^{3}C$\underline{H}_3$), 31.2 (OCH$_2$C$\underline{H}_2$CH$_2$Me), 41.6 (C^4), 49.3 (C^3), 55.8 (OMe), 58.3 (OC$\underline{H}_2$Me), 68.9 (OC$\underline{H}_2$CH$_2$CH$_2$Me), 76.4 (CH=), 109.7 (C^8), 111.5 (C^5), 120.5 (C^{8a}), 128.6 (C^{4a}), 147.2 (C^7), 151.6 (C^6), 155.4 (C^1), 171.0 (C=O). Found, %: C 69.03; H 8.47; N 3.98. $C_{20}H_{29}NO_4$. Calculated, %: C 69.14; H 8.41; N 4.03.

7-Butoxy-3,3-dimethyl-1-methylsulfanyl-6-methoxy-3,4-dihydroisoquinoline (VIb). Yield 0.77 g (25%), mp 69–70°C (EtOH). IR spectrum, cm^{-1}: 1600, 1566, 1516. ^{1}H NMR spectrum, δ, ppm: 0.97 t (3H, Me, *J* 7.4 Hz), 1.18 s (6H, 2Me), 1.49 m (2H, OCH$_2$CH$_2$C$\underline{H}_2$Me), 1.82 m (2H, OCH$_2$C$\underline{H}_2$CH$_2$Me), 2.40 s (3H, SMe), 2.60 s (2H, CH$_2$), 3.87 s (3H, OMe), 4.02 t (2H, OCH$_2$), 6.61 s (1H_{arom}), 7.16 s (1H_{arom}). ^{13}C NMR spectrum, δ, ppm: 12.0 (Me), 13.7 (SMe), 19.1(OCH$_2$CH$_2$C$\underline{H}_2$Me), 28.2 (C^{3}C$\underline{H}_3$), 31.1 (OCH$_2$C$\underline{H}_2$CH$_2$Me), 38.8 (C^4), 55.6 (C^3), 55.8 (OMe), 68.9 (OCH$_2$), 109.8 (C^8), 111.0 (C^5), 121.2 (C^{8a}), 129.1 (C^{4a}), 146.8 (C^7), 151.4 (C^6), 159.3 (C^1). Mass spectrum, *m/z* (I_{rel}, %): [*M*]$^+$ 307 (20), [*M* – Me]$^+$ 292 (100), 250 (15), 236 (11), 162 (10). Found, %: C 66.17; H 8.16; N 4.54; S 10.21. $C_{17}H_{25}NO_2S$. Calculated, %: C 66.41; H 8.20; N 4.56; S 10.43.

2-Methyl-1-(4-methoxyphenyl-3-propoxy)propan-1-ol (VIII). Yield 55%, mp 66–67°C (hexane). ^{1}H NMR spectrum, δ, ppm: 0.77 d (3H, Me, *J* 6.9 Hz), 0.99–1.05 m (6H, Me + OCH$_2$CH$_2$C$\underline{H}_2$Me), 1.80–1.95 m (4H, OH + CH + CH$_2$), 3.85 s (3H, OMe), 3.97 t (2H, OCH$_2$, *J* 7.1 Hz), 4.25 d (1H, CH, *J* 7.2 Hz), 6.81 s (2H_{arom}), 6.87 s (1H_{arom}). Mass spectrum, *m/z* (I_{rel}, %): [*M*]$^+$ 238 (12), 220 (19), 195 (100), 163 (14), 125 (38).

2-Butoxy-1-methoxy-4-(2-methylprop-1-enyl) benzene (IX). Yield 65%, bp 130°C (2 mm Hg). ^{1}H NMR spectrum, δ, ppm: 0.93–0.98 m (3H, Me), 1.41–1.54 m (2H, CH$_2$), 1.73–1.89 m (8H, 2Me + CH$_2$), 3.83 s (3H, OMe), 4.00 t (2H, OCH$_2$, *J* 6.8 Hz), 6.18 s (1H, CH), 6.70–6.82 m (3H_{arom}).

Ethyl [3,3-dimethyl-7-methoxy-6-propoxy-3,4-dihydroisoquinolin-1(2*H*)-ylidene]ethanoate (Xa). Yield 1.17 g (35%), mp 122–123°C (EtOH). IR spectrum, cm^{-1}: 3265, 1641, 1596, 1568, 1509. ^{1}H NMR spectrum, δ, ppm: 1.04 t (3H, Me, *J* 7.4 Hz), 1.26 s (6H, 2Me), 1.29 t (3H, OCH$_2$C$\underline{H}_3$), 1.87 m (2H, CH$_2$), 2.73 s (2H, CH$_2$), 3.87 s (3H, OMe), 3.99 t (2H, OCH$_2$, *J* 6.8 Hz), 4.15 q (2H, OC$\underline{H}_2$Me), 5.03 s (1H, CH=), 6.60 s (1H_{arom}), 7.12 s (1H_{arom}), 8.93 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 10.3 (Me), 14.6 (OCH$_2$C$\underline{H}_3$), 22.3 (OCH$_2$C$\underline{H}_2$Me), 28.4 (C^{3}C$\underline{H}_3$), 41.5 (C^4), 49.3 (C^3), 56.0 (OMe), 58.3 (OC$\underline{H}_2$Me), 70.3 (OCH$_2$), 76.3 (CH=), 108.3 (C^8), 112.3 (C^5), 120.4 (C^{8a}), 128.6 (C^{4a}), 147.8 (C^6), 150.8 (C^7), 155.5 (C^1), 171.0 (C=O). Mass spectrum, *m/z* (I_{rel}, %): [*M*]$^+$ 333 (51), [*M* – Me]$^+$ 318 (18), [*M* – OC$_2$H$_5$]$^+$ 288 (19), 273 (18), [*M* – OOC$_2$H$_5$]$^+$ 272 (100), 261 (30), 246 (40), 230 (12). Found, %: C 68.13; H 7.85; N 4.06. $C_{19}H_{27}NO_4$. Calculated, %: C 68.44; H 8.16; N 4.20.

3,3-Dimethyl-1-methylsulfanyl-7-methoxy-6-propoxy-3,4-dihydroisoquinoline (Xb). Yield 1.11 g (38%), mp 71–72.5°C (EtOH). IR spectrum, cm^{-1}: 1597, 1566, 1511. ^{1}H NMR spectrum, δ, ppm: 1.04 t (3H, Me, *J* 7.4 Hz), 1.18 s (6H, 2Me), 1.87 m (2H, CH$_2$), 2.41 s (3H, SMe), 2.60 s (2H, CH$_2$), 3.88 s (3H, OMe),

4.00 t (2H, OCH_2), 6.62 s ($1H_{arom}$), 7.16 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 10.3 (Me), 12.1 (SMe), 22.3 ($OCH_2\underline{C}H_2Me$), 28.2 ($C^3\underline{C}H_3$), 38.8 (C^4), 55.6 (C^3), 56.2 (OMe), 70.3 (OCH_2), 108.5 (C^8), 112.0 (C^5), 121.1 (C^{8a}), 129.2 (C^{4a}), 147.5 (C^7), 150.6 (C^6), 159.4 (C^1). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 293 (39), 279 (18), $[M - Me]^+$ 278 (100), 236 (24). Found, %: C 65.27; H 7.93; N 4.72; S 10.85. $C_{16}H_{23}NO_2S$. Calculated, %: C 65.49; H 7.90; N 4.77; S 10.93.

Ethyl [6-butoxy-3,3-dimethyl-7-methoxy-3,4-dihydroisoquinolin-1(2*H*)-ylidene]ethanoate (XIa). Yield 1.42 g (41%), mp 80–81°C (EtOH). IR spectrum, cm^{-1}: 3270, 1650, 1602, 1547, 1516. ^1H NMR spectrum, δ, ppm: 0.97 t (3H, Me, *J* 15.3 Hz), 1.25 s (6H, 2Me), 1.28 t (3H, $OCH_2\underline{Me}$, *J* 7.7 Hz), 1.49 m (2H, $OCH_2CH_2C\underline{H}_2Me$), 1.82 m (2H, $OCH_2C\underline{H}_2CH_2Me$), 2.71 s (2H, CH_2), 3.85 s (3H, OMe), 4.02 t (2H, OCH_2, *J* 6.9 Hz), 4.15 q (2H, $OC\underline{H}_2Me$), 5.03 s (1H, CH=), 6.60 s ($1H_{arom}$), 7.12 s ($1H_{arom}$), 8.92 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 13.7 (Me), 14.6 ($OCH_2\underline{C}H_3$), 19.0 ($OCH_2CH_2\underline{C}H_2Me$), 28.3 ($C^3\underline{C}H_3$), 31.0 ($OCH_2\underline{C}H_2CH_2Me$), 41.5 ($C^4$), 49.2 ($C^3$), 56.0 (OMe), 58.2 ($O\underline{C}H_2Me$), 68.5 ($OCH_2$), 76.4 (CH=), 108.4 ($C^8$), 112.4 ($C^5$), 120.4 ($C^{8a}$), 128.6 ($C^{4a}$), 147.9 ($C^6$), 150.9 ($C^7$), 155.4 ($C^1$), 171.0 (C=O). Found, %: C 69.07; H 8.45; N 3.92. $C_{20}H_{29}NO_4$. Calculated, %: C 69.14; H 8.41; N 4.03.

6-Butoxy-3,3-dimethyl-1-methylsulfanyl-7-methoxy-3,4-dihydroisoquinoline (XIb). Yield 1.54 g (50%), mp 53–55°C (EtOH). IR spectrum, cm^{-1}: 1594, 1560, 1514. ^1H NMR spectrum, δ, ppm: 0.96 t (3H, Me, *J* 7.4 Hz), 1.18 s (6H, 2Me), 1.48 m (2H, $OCH_2CH_2C\underline{H}_2Me$), 1.82 m (2H, $OCH_2C\underline{H}_2CH_2Me$), 2.40 s (3H, SMe), 2.59 s (2H, CH_2), 3.86 s (3H, OMe), 4.02 t (2H, OCH_2, *J* 6.8 Hz), 6.62 s ($1H_{arom}$), 7.15 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 12.0 (Me), 13.7 (SMe), 19.0 ($OCH_2CH_2\underline{C}H_2Me$), 28.2 ($C^3\underline{C}H_3$), 31.0 ($OCH_2\underline{C}H_2CH_2Me$), 38.8 ($C^4$), 55.6 ($C^3$), 56.1 (OMe), 68.5 ($OCH_2$), 108.3 ($C^8$), 111.9 ($C^5$), 120.9 ($C^{8a}$), 129.1 ($C^{4a}$), 147.4 ($C^7$), 150.5 ($C^6$), 159.3 ($C^1$). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 307 (25), $[M - Me]^+$ 292 (100), 250 (13), 236 (25), 162 (14). Found, %: C 66.11; H 8.29; N 4.62; S 10.21. $C_{17}H_{25}NO_2S$. Calculated, %: C 66.41; H 8.20; N 4.56; S 10.43.

Ethyl [3,3-dimethyl-6,7-diethoxy-3,4-dihydroisoquinolin-1(2*H*)-ylidene]ethanoate (XIIa). Yield 1.73 g (52%), mp 71–72°C (EtOH). IR spectrum, cm^{-1}: 1715, 1640, 1590, 1560, 1505. ^1H NMR spectrum, δ, ppm: 1.20 s (6H, 2Me), 1.22 m (3H, $OCH_2\underline{Me}$), 1.39 q (6H, 2Me), 2.67 s (2H, CH_2), 4.04 m (6H, $2OCH_2$ + $OC\underline{H}_2Me$), 4.95 s (1H, CH=), 6.54 s ($1H_{arom}$), 7.08 s ($1H_{arom}$), 8.87 br.s (H, NH). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 333 (57), $[M - Me]^+$ 318 (20), $[M - OC_2H_5]^+$ 288 (17), 272 (100), 261 (31), 248 (34), 232 (13). Found, %: C 68.37; H 8.21; N 4.25. $C_{19}H_{27}NO_4$. Calculated, %: C 68.44; H 8.16; N 4.20.

3,3-Dimethyl-1-methylsulfanyl-6,7-diethoxy-3,4-dihydroisoquinoline (XIIb). Yield 1.17 g (40%), mp 71–73°C (EtOH). IR spectrum, cm^{-1}: 1660, 1596, 1566, 1514. ^1H NMR spectrum, δ, ppm: 1.17 s (6H, 2Me), 1.44 m (6H, 2Me), 2.40 s (3H, SMe), 2.59 s (2H, CH_2), 4.09 m (4H, $2OCH_2$), 6.61 s ($1H_{arom}$), 7.16 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 12.0 (SMe), 14.6 (Me), 14.7 (Me), 28.2 ($C^3\underline{C}H_3$), 38.8 (C^4), 55.6 (C^3), 64.3 (OCH_2), 64.8 (OCH_2), 110.5 (C^5), 112.4 (C^8), 121.2 (C^{8a}), 129.3 (C^{4a}), 146.8 (C^7), 150.9 (C^6), 159.3 (C^1). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 293 (27), $[M - Me]^+$ 278 (100), 265 (15). Found, %: C 65.65; H 7.79; N 4.63; S 10.74. $C_{16}H_{23}NO_2S$. Calculated, %: C 65.49; H 7.90; N 4.77; S 10.93.

Ethyl [3,3-dimethyl-6,7-dipropoxy-3,4-dihydroisoquinolin-1(2*H*)-ylidene]ethanoate (XIIIa). Yield 1.41 g (39%), mp 93–94°C (EtOH). IR spectrum, cm^{-1}: 1700, 1596, 1564, 1516. ^1H NMR spectrum, δ, ppm: 1.04 t (6H, 2Me, *J* 7.5 Hz), 1.26 s (6H, 2Me), 1.27 t (3H, $OCH_2\underline{Me}$, *J* 7.5 Hz), 1.84 m (4H, $2CH_2$), 2.71 s (2H, CH_2), 3.95 m (4H, $2OCH_2$), 4.14 q (2H, $OC\underline{H}_2Me$), 5.00 s (1H, CH=), 6.59 s ($1H_{arom}$), 7.14 s ($1H_{arom}$), 8.92 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 10.3 (2C, Me), 14.6 ($OCH_2\underline{C}H_3$), 22.4 ($OCH_2\underline{C}H_2Me$), 22.6 ($OCH_2\underline{C}H_2Me$), 28.4 ($C^3\underline{C}H_3$), 41.5 (C^4), 49.3 (C^3), 58.3 ($O\underline{C}H_2Me$), 70.3 (OCH_2), 71.0 (OCH_2), 76.3 (CH=), 110.8 (C^8), 113.0 (C^5), 120.5 (C^{8a}), 128.8 (C^{4a}), 147.5 (C^7), 151.5 (C^6), 155.5 (C^1), 171.0 (C=O). Found, %: C 69.89; H 8.59; N 3.98. $C_{21}H_{31}NO_4$. Calculated, %: C 69.78; H 8.64; N 3.87.

3,3-Dimethyl-1-methylsulfanyl-6,7-dipropoxy-3,4-dihydroisoquinoline (XIIIb). Yield 1.06 g (33%), mp 54–57°C (EtOH). IR spectrum, cm^{-1}: 1596, 1564, 1516. ^1H NMR spectrum, δ, ppm: 1.03 t (6H, 2Me, *J* 7.2 Hz), 1.17 s (6H, 2Me), 1.81 m (4H, $2OCH_2C\underline{H}_2Me$), 2.39 s (3H,SMe), 2.58 s (2H, CH_2), 3.96 t (4H, $2OCH_2$, *J* 6.6 Hz), 6.60 s ($1H_{arom}$), 7.17 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 10.4 (2C, Me), 12.0 (SMe), 22.5 ($OCH_2\underline{C}H_2CH_3$), 22.6 ($OCH_2\underline{C}H_2Me$), 28.3 ($C^3\underline{C}H_3$), 38.9 ($C^4$), 55.7 ($C^3$), 70.5 ($OCH_2$), 71.2 ($OCH_2$), 111.1 ($C^5$), 112.9 ($C^8$), 121.3 ($C^{8a}$), 129.5 ($C^{4a}$), 147.3 ($C^7$), 151.4 ($C^6$), 159.4 ($C^1$). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$

321 (26), $[M - Me]^+$ 306 (100), $[M - C_3H_7]^+$ 278 (15), 264 (12), 222 (13). Found, %: C 66.92; H 8.50; N 4.40; S 9.77. $C_{18}H_{27}NO_2S$. Calculated, %: C 67.25; H 8.47; N 4.36; S 9.97.

Ethyl [6,7-dibutoxy-3,3-dimethyl-3,4-dihydroisoquinolin-1(2*H*)-ylidene]ethanoate (XIVa). Yield 0.47 g (12%), mp 72–73°C (EtOH). IR spectrum, cm^{-1}: 1648, 1602, 1572, 1516. ^1H NMR spectrum, δ, ppm: 0.92 t (6H, 2Me, *J* 7.2 Hz), 1.21 s (6H, 2Me), 1.24 t (3H, $OCH_2\underline{Me}$, *J* 7.7 Hz), 1.44 m (4H, $2OCH_2CH_2C\underline{H}_2Me$), 1.74 m (4H, $2OCH_2C\underline{H}_2CH_2Me$), 2.67 s (2H, CH_2), 3.94 m (4H, $2OCH_2$), 4.09 q (2H, $OC\underline{H}_2Me$), 4.95 s (1H, CH=), 6.54 s ($1H_{arom}$), 7.08 s ($1H_{arom}$), 8.88 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 13.7 (2C, Me), 14.6 ($OCH_2\underline{C}H_3$), 19.1 (2C, $OCH_2CH_2\underline{C}H_2Me$), 28.3 ($C^3\underline{C}H_3$), 31.1 ($OCH_2\underline{C}H_2CH_2Me$), 31.2 ($OCH_2\underline{C}H_2CH_2Me$), 41.5 ($C^4$), 49.2 ($C^3$), 58.2 ($O\underline{C}H_2Me$), 68.6 ($OCH_2$), 69.2 ($OCH_2$), 76.3 (CH=), 110.7 ($C^8$), 113.0 ($C^5$), 120.5 ($C^{8a}$), 128.7 ($C^{4a}$), 147.6 ($C^7$), 151.5 ($C^6$), 155.5 ($C^1$), 171.0 (C=O). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 389 (66), $[M - Me]^+$ 374 (24), $[M - OC_2H_5]^+$ 344 (16), 328 (100), $[M - COOC_2H_5]^+$ 317 (48), $[M - OC_4H_9]^+$ 316 (12), 302 (30), 272 (16). Found, %: C 70.85; H 9.10; N 3.57. $C_{23}H_{35}NO_4$. Calculated, %: C 70.92; H 9.06; N 3.60.

6,7-Dibutoxy-3,3-dimethyl-1-methylsulfanyl-3,4-dihydroisoquinoline (XIVb). Yield 0.52 g (15%), mp 41–43°C (EtOH). IR spectrum, cm^{-1}: 1585, 1550, 1505. ^1H NMR spectrum, δ, ppm: 0.97 t (6H, 2Me, *J* 7.4 Hz), 1.17 s (6H, 2Me), 1.50 m (4H, $2OCH_2CH_2C\underline{H}_2Me$), 1.80 m (4H, $2OCH_2C\underline{H}_2CH_2Me$), 2.40 s (3H, SMe), 2.59 s (2H, CH_2), 4.00 t (4H, $2OCH_2$, *J* 5.9 Hz), 6.60 s ($1H_{arom}$), 7.15 s ($1H_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 349 (23), $[M - Me]^+$ 334 (100), $[M - C_4H_9]^+$ 292 (18), 278 (16), 222 (15). ^{13}C NMR spectrum, δ, ppm: 11.9 (Me), 13.7 (SMe), 19.1 (2C, $OCH_2CH_2\underline{C}H_2Me$), 28.2 ($C^3\underline{C}H_3$), 31.1 ($OCH_2\underline{C}H_2CH_2Me$), 31.2 ($OCH_2\underline{C}H_2CH_2Me$), 38.8 ($C^4$), 55.5 ($C^3$), 68.6 ($OCH_2$), 69.2 ($OCH_2$), 110.9 ($C^8$), 112.7 ($C^5$), 121.2 ($C^{8a}$), 129.3 ($C^{4a}$), 147.2 ($C^6$), 151.3 ($C^7$), 159.3 ($C^1$). Found, %: C 68.82; H 8.78; N 4.08; S 9.06. $C_{20}H_{31}NO_2S$. Calculated, %: C 68.72; H 8.94; N 4.01; S 9.17.

Ethyl [6,7-dibutoxy-3,3-pentamethylene-3,4-dihydroisoquinolin-1(2*H*)-ylidene]ethanoate (XVa). Yield 0.39 g (9%), mp 97–100°C (EtOH). IR spectrum, cm^{-1}: 3244, 3124, 1722, 1634, 1600, 1570, 1514. ^1H NMR spectrum, δ, ppm: 0.92 t (6H, 2Me, *J* 7.7 Hz), 1.25 t (7H, $OCH_2\underline{Me}$ + $2OCH_2CH_2C\underline{H}_2Me$, *J* 7.1 Hz), 1.38–1.55 m (10H, $5CH_2$), 1.75 m (4H, $2OCH_2C\underline{H}_2CH_2Me$), 2.68 s (2H, CH_2), 3.94 m (4H, $2OCH_2$), 4.11 q (2H, $OC\underline{H}_2Me$), 4.96 s (1H, CH=), 6.55 s ($1H_{arom}$), 7.07 s ($1H_{arom}$), 9.33 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 13.6 (Me), 13.7 (Me), 14.6 ($OCH_2\underline{C}H_3$), 19.1 ($OCH_2CH_2\underline{C}H_2Me$), 21.7 ($C^3\underline{C}H_2$), 25.5 ($C^3\underline{C}H_2$), 31.1 ($OCH_2\underline{C}H_2CH_2Me$), 31.2 ($OCH_2\underline{C}H_2CH_2Me$), 36.3 ($C^3\underline{C}H_2$), 40.3 ($C^4$), 50.9 ($C^3$), 58.2 ($O\underline{C}H_2Me$), 68.6 ($OCH_2$), 69.2 ($OCH_2$), 76.3 (CH=), 110.7 ($C^8$), 113.1 ($C^5$), 120.7 ($C^{8a}$), 128.4 ($C^{4a}$), 147.5 ($C^7$), 151.5 ($C^6$), 155.3 ($C^1$), 171.1 (C=O). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 429 (100), 386 (22), $[M - OC_2H_5]^+$ 384 (10), $[M - OC_4H_9]^+$ 357 (31), 341 (13), 340 (39), 328 (10), 327 (37). Found, %: C 72.75; H 9.12; N 3.22. $C_{26}H_{39}NO_4$. Calculated, %: C 72.69; H 9.15; N 3.26.

Ethyl [7-hydroxy-6-propoxy-3,3-dimethyl- 3,4-dihydroisoquinolin-1(2*H*)-ylidene]ethanoate (XVIa). Yield 0.10 g (3%), mp 132–141°C (EtOH). IR spectrum, cm^{-1}: 3300, 3210, 1628, 1575. ^1H NMR spectrum, δ, ppm: 0.99 t (3H, Me, *J* 7.5 Hz), 1.20 s (6H, 2Me), 1.23 t (3H, $OCH_2C\underline{H}_3$, *J* 7.5 Hz), 1.80 m (2H, $OCH_2C\underline{H}_2Me$), 2.66 s (2H, CH_2), 3.96 m (2H, OCH_2), 4.07 q (2H, $OC\underline{H}_2Me$), 4.96 s (1H, CH=), 5.51 br.s (1H, OH), 6.52 s ($1H_{arom}$), 7.17 s ($1H_{arom}$), 8.86 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 10.4 (Me), 14.7 ($OCH_2\underline{C}H_3$), 22.5 ($OCH_2\underline{C}H_2Me$), 28,5 ($C^3\underline{C}H_3$), 41.9 (C^4), 49,4 (C^3), 58.4 ($O\underline{C}H_2Me$), 70.5 (OCH_2), 77.0 (CH=), 111.3 (C^8), 111.3 (C^5), 121.4 (C^{8a}), 127.9 (C^{4a}), 144.4 (C^7), 148.0 (C^6), 155.3 (C^1), 171.4 (C=O). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 319 (56), $[M - Me]^+$ 304 (26), $[M - OC_2H_5]^+$ 274 (17), 258 (100), 232 (41). Found, %: C 67.81; H 7.93; N 4.34. $C_{18}H_{25}NO_4$. Calculated, %: C 67.69; H 7.89; N 4.39.

Ethyl [6-butoxy-7-hydroxy-3,3-dimethyl-3,4-dihydroisoquinolin-1(2*H*)-ylidene]ethanoate (XVIIa). Yield 0.07 g (2%), mp 141–145°C (EtOH). IR spectrum, cm^{-1}: 3340, 3292, 1684, 1636, 1594. ^1H NMR spectrum, δ, ppm: 0.97 t (3H, Me, *J* 7.4 Hz), 1.24 s (6H, 2Me), 1.27 m (3H, $OCH_2C\underline{H}_3$), 1.44–1.54 m (2H, $OCH_2CH_2C\underline{H}_2Me$), 1.74–1.84 m (2H, $OCH_2C\underline{H}_2CH_2Me$), 2.69 s (2H, CH_2), 4.04 t (2H, OCH_2, *J* 6.6 Hz), 4.09–4.16 q (2H, $OC\underline{H}_2Me$), 5.01 s (1H, CH=), 5.82 br.s (1H, OH), 6.57 s ($1H_{arom}$), 7.22 s ($1H_{arom}$), 8.91 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 13.7 (Me), 14.6 ($OCH_2\underline{C}H_3$), 19.1 ($OCH_2CH_2\underline{C}H_2Me$), 28.3 ($C^3\underline{C}H_3$), 31.0 ($OCH_2\underline{C}H_2CH_2Me$), 41.6 ($C^4$), 49.3 ($C^3$), 58.3 ($O\underline{C}H_2Me$), 68.5 ($OCH_2$), 76.6 (CH=), 111.1 ($C^8$), 111.2 ($C^5$), 121.0 ($C^{8a}$), 127.8 ($C^{4a}$), 144.2 ($C^7$), 148.1 ($C^6$), 155.3 ($C^1$), 171.2 (C=O). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 333 (45), $[M - Me]^+$ 318 (21), $[M - OC_2H_5]^+$ 288 (18), 272 (100), 260 (11), 246 (34). Found, %: C 68.35;

H 8.07; N 4.24. $C_{19}H_{27}NO_4$. Calculated, %: C 68.44; H 8.16; N 4.20.

6-Butoxy-3,3-dimethyl-1-methylsulfanyl-3,4-dihydroisoquinolin-7-ol (XVIIb. Yield 0.03 g (1%), mp 95–100°C (EtOH). IR spectrum, cm^{-1}: 1594, 1560, 1514. ^1H NMR spectrum, δ, ppm: 0.98 t (3H, CH_3, *J* 7.4 Hz), 1.17 s (6H, 2Me), 1.49 m (2H, $OCH_2CH_2C\underline{H}_2Me$), 1.80 m (2H, $OCH_2C\underline{H}_2CH_2Me$), 2.58 s (2H, CH_2), 2.39 s (3H, SMe), 4.06 m (2H, OCH_2), 5.50 br.s (1H, OH), 6.58 s ($1H_{arom}$), 7.24 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 12.2 (Me), 13.8 (SMe), 19.2 ($OCH_2CH_2\underline{C}H_2Me$), 28.3 ($C^3\underline{C}H_3$), 31.2 ($OCH_2\underline{C}H_2CH_2Me$), 39.1 ($C^4$), 55.8 ($C^3$), 68.7 ($OCH_2$), 110.9 ($C^5$), 111.1 ($C^8$), 121.8 ($C^{8a}$), 128.4 ($C^{4a}$), 144.0 ($C^7$), 147.9 ($C^6$), 159.9 ($C^1$). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 293 (37), $[M - Me]^+$ 278 (100), $[M - C_4H_9]^+$ 236 (9), 222 (35). Found, %: C 65.53; H 7.87; N 4.80; S 10.82. $C_{16}H_{23}NO_2S$. Calculated, %: C 65.49; H 7.90; N 4.77; S 10.93.

Ethyl [6-butoxy-7-hydroxy-3,3-pentamethylene-3,4-dihydroisoquinolin-1(2*H*)-ylidene]ethanoate (XVIIIa). Yield 0.04 g (1%), mp 127–135°C (hexane). ^1H NMR spectrum, δ, ppm: 0.98 t (3H, Me, *J* 7.4 Hz), 1.30 t (3H, $OCH_2\underline{Me}$, *J* 6.9 Hz), 1.37–1.60 m (12H, $5CH_2$ + $OCH_2CH_2C\underline{H}_2Me$), 1.81 m (2H, $OCH_2C\underline{H}_2CH_2Me$), 2.71 s (2H, CH_2), 4.05 t (2H, OCH_2, *J* 6.6 Hz), 4.14 q (2H, $OC\underline{H}_2Me$), 5.02 s (1H, CH=), 5.47 br.s (1H, OH), 6.56 s ($1H_{arom}$), 7.20 s ($1H_{arom}$), 9.25 br.s (1H, NH). Mass spectrum of thermolysis product, *m/z* (I_{rel}, %): $[M]^+$ 301 (48), $[M - Me]^+$ 286 (10), 258 (100), 245 (25). Found, %: C 70.63; H 8.41; N 3.71. $C_{22}H_{31}NO_4$. Calculated, %: C 70.75; H 8.37; N 3.75.

1,3,3-Trimethyl-6-methoxy-7-ethoxy-3,4-dihydroisoquinoline (XIXa). Yield 1.63 g (66%), mp 80–82°C (hexane). IR spectrum, cm^{-1}: 1622, 1606, 1572, 1516. ^1H NMR spectrum, δ, ppm: 1.18 s (2H, 2Me), 1.46 t (3H, $OCH_2C\underline{H}_3$, *J* 6.9 Hz), 2.32 s (3H, Me), 2.60 s (2H, CH_2), 3.89 s (3H, OMe), 4.10 q (2H, OCH_2), 6.62 s ($1H_{arom}$), 6.99 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 14.8 ($OCH_2\underline{C}H_3$), 23.2 (Me), 27.9 ($C^3\underline{C}H_3$), 38.6 (C^4) , 53.5 (C^3), 55.8 (OMe), 64.9 (OCH_2), 111.1 (C^8), 111.2 (C^5), 121.4 (C^{8a}), 130.1 (C^{4a}), 146.5 (C^7), 151.4 (C^6), 160.6 (C^1). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 247 (100), $[M - Me]^+$ 232 (74), $[M - C_2H_5]^+$ 218 (11), 205 (36). Found, %: C 72.71; H 8.63; N 5.61. $C_{15}H_{21}NO_2$. Calculated, %: C 72.84; H 8.56; N 5.66.

1,3,3-Trimethyl-6-methoxy-7-propoxy-3,4-dihydroisoquinoline (XIXb). Yield 2.11 g (81%), mp 58–60°C (ethyl ether). IR spectrum, cm^{-1}: 1768, 1628, 1606, 1574, 1516. ^1H NMR spectrum, δ, ppm: 1.04 t (3H, Me, *J* 7.2 Hz), 1.17 s (2H, 2Me), 1.85 m (2H, $OCH_2C\underline{H}_2Me$), 2.32 s (3H, Me), 2.59 s (2H, CH_2), 3.88 s (3H, OMe), 3.97 t (2H, OCH_2, *J* 6.8 Hz), 6.62 s ($1H_{arom}$), 6.99 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 10.3 ($OCH_2CH_2\underline{C}H_3$), 22.7 ($OCH_2\underline{C}H_2Me$), 23.1 (Me), 28.0 ($C^3\underline{C}H_3$), 38.8 ($C^4$), 53.6 ($C^3$), 56.1(OMe), 71.7 ($OCH_2$), 112.0 ($C^5$), 112.3($C^8$), 121.8 ($C^{8a}$), 130.4 ($C^{4a}$), 147.2 ($C^7$), 152.1 ($C^6$), 160.4 ($C^1$). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 261 (100), $[M - Me]^+$ 246 (99), $[M - C_3H_7]^+$ 219 (43), 204 (95). Found, %: C 73.41; H 8.95; N 5.29. $C_{16}H_{23}NO_2$. Calculated, %: C 73.53; H 8.87; N 5.36.

7-Butoxy-1,3,3-trimethyl-6-methoxy-3,4-dihydroisoquinoline (XIXc). Yield 2.45 g (89%), mp 50–56°C (hexane). IR spectrum, cm^{-1}: 1628, 1604, 1574, 1516. ^1H NMR spectrum, δ, ppm: 0.98 t (3H, Me, *J* 7.4 Hz), 1.18 s (2H, 2Me), 1.50 m (2H, $OCH_2CH_2C\underline{H}_2Me$), 1.80 m (2H, $OCH_2C\underline{H}_2CH_2Me$), 2.33 s (3H, Me), 2.60 s (2H, CH_2), 3.88 s (3H, OMe), 4.01 t (2H, OCH_2, *J* 6.8 Hz), 6.62 s ($1H_{arom}$), 6.99 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 13.8 ($OCH_2CH_2CH_2\underline{C}H_3$), 19.2 ($OCH_2CH_2\underline{C}H_2Me$), 23.4 (Me), 28.0 ($C^3\underline{C}H_3$), 31.4 ($OCH_2\underline{C}H_2CH_2Me$), 38.6 ($C^4$), 53.5 ($C^3$), 56.0 (OMe), 69.4 ($OCH_2$), 111.3 ($C^8$), 111.4 ($C^5$), 121.6 ($C^{8a}$), 130.1 ($C^{4a}$), 146.9 ($C^7$), 151.6 ($C^6$), 160.6 ($C^1$). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 275 (100), $[M - Me]^+$ 260 (53), 233 (15), $[M - C_4H_9]^+$ 218 (11), 204 (56). Found, %: C 74.01; H 9.11; N 5.12. $C_{17}H_{25}NO_2$. Calculated, %: C 74.14; H 9.15; N 5.09.

1,3,3-Trimethyl-6,7-diethoxy-3,4-dihydroisoquinoline (XIXf). Yield 1.64 g (63%), mp 93–96°C (hexane). IR spectrum, cm^{-1}: 1602, 1560, 1505. ^1H NMR spectrum, δ, ppm: 1.12 s (2H, 2Me), 2.53 s (2H, CH_2), 1.39 m (6H, $2OCH_2C\underline{H}_3$), 2.26 s (3H, Me), 4.05 m (4H, $2OCH_2$), 6.57 s ($1H_{arom}$), 6.95 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 14.4 ($OCH_2\underline{C}H_3$), 14.3 ($OCH_2\underline{C}H_3$), 22.8 (Me), 27.5 ($C^3\underline{C}H_3$), 38.1 (C^4), 53.0 (C^3), 64.8 (OCH_2), 63.9 (OCH_2), 111.8 (C^5), 112.3 (C^8), 121.0 (C^{8a}), 129.8 (C^{4a}), 146.4 (C^7), 150.7 (C^6), 160.0 (C^1). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 261 (100), $[M - Me]^+$ 246 (47), $[M - C_2H_5]^+$ 232 (42), 219 (28), 204 (15), 190 (16). Found, %: C 73.70; H 8.81; N 5.42. $C_{16}H_{23}NO_2$. Calculated, %: C 73.53; H 8.87; N 5.36.

1,3,3-Trimethyl-6,7-dipropoxy-3,4-dihydroisoquinoline (XIXg). Yield 1.71 g (59%), light-yellow oily substance. IR spectrum, cm^{-1}: 1636, 1600, 1560, 1516. ^1H NMR spectrum, δ, ppm: 1.04 t (6H, 2Me, *J* 7.4 Hz), 1.17 s (6H, 2Me), 1.84 m (4H, $2CH_2$), 2.32 s

(3H, Me), 2.58 s (2H, CH_2), 3.97 q (4H, $2OCH_2$), 6.61 s ($1H_{arom}$), 7.00 s ($1H_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 289 (100), $[M - Me]^+$ 274 (95), $[M - C_3H_7]^+$ 246 (89), 232 (46), 204 (73), 190 (94). Found, %: C 74.55; H 9.47; N 5.00. $C_{18}H_{27}NO_2$. Calculated, %: C 74.70; H 9.40; N 4.84.

1,3,3-Trimethyl-6-propoxy-3,4-dihydroisoquinolin-7-ol (XIXi). Yield 0.05 g (2%), mp 145–153°C (hexane). ^1H NMR spectrum, δ, ppm: 0.99 t (3H, Me, *J* 7.4 Hz), 1.14 s (6H, 2Me), 1.80 m (2H, CH_2), 2.25 s (3H, Me), 2.54 s (2H, CH_2), 4.05 t (2H, OCH_2), 6.55 s ($1H_{arom}$), 7.04 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 10.4 (Me), 22.5 ($OCH_2\underline{C}H_2Me$), 23.3 (Me), 28.0 ($C^3\underline{C}H_3$), 38.8 (C^4), 53.7 (C^3), 70.5 (OCH_2), 111.2 (C^5), 112.0 (C^8), 121.9 (C^{8a}), 129.0 (C^{4a}), 147.8 (C^6), 144.1 (C^7), 159.8 (C^1). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 247 (95), $[M - Me]^+$ 232 (33), $[M - C_3H_7]^+$ 204 (100), 190 (47), 163 (34). Found, %: C 72.94; H 8.39; N 5.71. $C_{15}H_{21}NO_2$. Calculated, %: C 72.84; H 8.56; N 5.66.

6-Butoxy-1,3,3-trimethyl-3,4-dihydroisoquinolin-7-ol (XIXj). Yield 0.05 g (2%), mp 91–110°C (hexane). IR spectrum, cm^{-1}: 1620, 1580, 1512. ^1H NMR spectrum, δ, ppm: 0.92 t (3H, Me, *J* 7.4 Hz), 1.14 s (6H, 2Me), 1.43 m (2H, $OCH_2CH_2C\underline{H}_2Me$), 1.74 m (2H, $OCH_2C\underline{H}_2CH_2Me$), 2.29 s (3H, Me), 2.53 s (2H, CH_2), 3.97 t (2H, OCH_2), 6.59 s ($1H_{arom}$), 6.88 s ($1H_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 261 (42), $[M - Me]^+$ 246 (18), $[M - C_4H_9]^+$ 204 (45), 190 (37), 163 (34), 149 (25). Found, %: C 73.44; H 8.91; N 5.42. $C_{16}H_{23}NO_2$. Calculated, %: C 73.53; H 8.87; N 5.36.

3,3-Dimethyl-6-methoxy-7-ethoxy-3,4-dihydroisoquinolin-1(2*H*)-one (XXa). Yield 1.99 g (80%), mp 196–198°C (EtOH). IR spectrum, cm^{-1}: 1662, 1604, 1516. ^1H NMR spectrum, δ, ppm: 1.29 c (6H, 2Me), 1.44 t (3H, Me, *J* 7.2 Hz), 2.83 s (2H, CH_2), 3.90 s (3H, OMe), 4.14 q (2H, OCH_2), 5.54 br.s (1H, NH), 6.61 s ($1H_{arom}$), 7.55 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 14.7 (Me), 28.8 ($C^3\underline{C}H_3$), 41.3 (C^4), 52.1 (C^3), 56.0 (OMe), 64.4 (OCH_2), 110.3 (C^8), 111.4 (C^5), 120.3 (C^{8a}), 131.0 (C^{4a}), 147.2 (C^7), 152.5 (C^6), 165.5 (C^1). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 249 (82), $[M - Me]^+$ 234 (100), $[M - C_3H_7]^+$ 206 (23), 192 (74). Found, %: C 67.59; H 7.62; N 5.66. $C_{14}H_{19}NO_3$. Calculated, %: C 67.45; H 7.68; N 5.62.

3,3-Dimethyl-6-methoxy-7-propoxy-3,4-dihydroisoquinolin-1(2*H*)-one (XXb). Yield 2.24 g (85%), mp 182–185°C (EtOH). IR spectrum, cm^{-1}: 1660, 1606, 1516. ^1H NMR spectrum, δ, ppm: 1.02 t (3H, Me, *J* 7.2 Hz), 1.29 s (6H, 2Me), 1.84 m (2H, CH_2), 2.83 s (2H, CH_2), 3.89 s (3H, OCH_3), 4.02 t (2H, OCH_2, *J* 6.8 Hz), 5.53 br.s (1H, NH), 6.61 s ($1H_{arom}$), 7.55 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 10.3 (Me), 22.3 ($OCH_2\underline{C}H_2Me$), 28.7 ($C^3\underline{C}H_3$), 41.2 (C^4), 52.0 (C^3), 55.9 (OMe), 70.4 (OCH_2), 110.4 (C^8), 111.5 (C^5), 120.3 (C^{8a}), 131.0 (C^{4a}), 147.3 (C^7), 152.5 (C^6), 165.5 (C^1). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 263 (81), $[M - Me]^+$ 248 (62), 206 (100), 164 (44). Found, %: C 68.29; H 8.11; N 5.27. $C_{15}H_{21}NO_3$. Calculated, %: C 68.42; H 8.04; N 5.32.

7-Butoxy-3,3-dimethyl-6-methoxy-3,4-dihydroisoquinolin-1(2*H*)-one (XXc). Yield 1.55 g (56%), mp 150–153°C (EtOH). IR spectrum, cm^{-1}: 3180, 1654, 1602, 1516. ^1H NMR spectrum, δ, ppm: 0.96 t (3H, Me, *J* 7.4 Hz), 1.29 s (6H, 2Me), 1.47 m (2H, $OCH_2CH_2C\underline{H}_2Me$), 1.82 m (2H, $OCH_2C\underline{H}_2CH_2Me$), 2.83 s (2H, CH_2), 3.89 s (3H, OMe), 4.06 t (2H, OCH_2, *J* 6.8 Hz), 5.53 br.s (1H, NH), 6.61 s ($1H_{arom}$), 7.55 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 13.6 (Me), 19.0 ($OCH_2CH_2\underline{C}H_2Me$), 28.6 ($C^3\underline{C}H_3$), 31.0 ($OCH_2\underline{C}H_2CH_2Me$), 41.1 ($C^4$), 51.9 ($C^3$), 55.8 (OMe), 68.6 ($OCH_2$), 110.3 ($C^8$), 111.4 ($C^5$), 120.3 ($C^{8a}$), 130.9 ($C^{4a}$), 147.3 ($C^7$), 152.4 ($C^6$), 165.5 ($C^1$). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 277 (72), $[M - Me]^+$ 262 (39), $[M - C_4H_9]^+$ 220 (47), 206 (100), 192 (10), 164 (56). Found, %: C 69.19; H 8.42; N 5.01. $C_{16}H_{23}NO_3$. Calculated, %: C 69.29; H 8.36; N 5.05.

6-Propoxy-3,3-dimethyl-7-methoxy-3,4-dihydroisoquinolin-1(2*H*)-one (XXd). Yield 0.10 g (38%), mp 173–174°C (EtOH). IR spectrum, cm^{-1}: 3217, 1659, 1604, 1512. ^1H NMR spectrum, δ, ppm: 1.05 t (3H, Me, *J* 7.4 Hz), 1.31 s (6H, 2Me), 1.89 m (2H, $OCH_2C\underline{H}_2Me$), 2.82 s (2H, CH_2), 3.91 s (3H, OMe), 4.01 t (2H, OCH_2, *J* 6.6 Hz), 6.27 br.s (1H, NH), 6.63 s ($1H_{arom}$), 7.55 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 10.3 (Me), 22.2 ($OCH_2\underline{C}H_2Me$), 28.7 ($C^3\underline{C}H_3$), 41.1 (C^4), 52.1 (C^3), 56.0 (OMe), 70.3 (OCH_2), 110.2 (C^8), 111.1 (C^5), 120.0 (C^{8a}), 131.1 (C^{4a}), 148.0 (C^7), 151.7 (C^6), 165.6 (C^1). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 263 (48), $[M - Me]^+$ 248 (38), 206 (100), 164 (22), 136 (23). Found, %: C 68.31; H 7.99; N 5.30. $C_{15}H_{21}NO_3$. Calculated, %: C 68.42; H 8.04; N 5.32.

6-Butoxy-3,3-dimethyl-7-methoxy-3,4-dihydroisoquinolin-1(2*H*)-one (XXe). Yield 1.80 g (65%), mp 138–139°C (EtOH). IR spectrum, cm^{-1}: 3165, 1656, 1599, 1511. ^1H NMR spectrum, δ, ppm: 0.97 t (3H, Me, *J* 7.4 Hz), 1.31 s (6H, 2Me), 1.49 m (2H, $OCH_2CH_2C\underline{H}_2Me$), 1.84 m (2H, $OCH_2C\underline{H}_2CH_2Me$),

2.82 s (2H, CH_2), 3.90 s (3H, OMe), 4.04 t (2H, OCH_2, *J* 6.6 Hz), 6.56 br.s (1H, NH), 6.64 s ($1H_{arom}$), 7.55 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 13.7 (Me), 19.0 ($OCH_2CH_2\underline{C}H_2Me$), 28.6 ($C^3\underline{C}H_3$), 30.9 ($OCH_2\underline{C}H_2CH_2Me$), 41.1 ($C^4$), 52.0 ($C^3$), 56.0 (OMe), 68.5 ($OCH_2$), 110.2 ($C^8$), 111.1 ($C^5$), 120.0 ($C^{8a}$), 131.1 ($C^{4a}$), 147.9 ($C^7$), 151.8 ($C^6$), 165.6 ($C^1$). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 277 (59), $[M - Me]^+$ 262 (38), $[M - C_4H_9]^+$ 220 (43), 206 (100), 164 (38). Найде-но, %: C 69.36; H 8.32; N 4.99. $C_{16}H_{23}NO_3$. Calculated, %: C 69.29; H 8.36; N 5.05.

3,3-Dimethyl-6,7-diethoxy-3,4-dihydroisoquinolin-1(2*H*)-one (XXf). Yield 1.97 g (75%), mp 192–193°C (EtOH). IR spectrum, cm^{-1}: 1756, 1660, 1604, 1514. ^1H NMR spectrum, δ, ppm: 1.29 s (6H, 2Me), 1.46 q (6H, $2OCH_2\underline{Me}$), 2.81 s (2H, CH_2), 4.12 m (4H, $2OCH_2$), 5.57 br.s (1H, NH), 6.61 s ($1H_{arom}$), 7.53 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 14.6 (Me), 14.7 (Me), 28.8 ($C^3\underline{C}H_3$), 41.2 (C^4), 52.0 (C^3), 64.4 (OCH_2), 64.5 (OCH_2), 111.7 (C^8), 111.9 (C^5), 120.2 (C^{8a}), 131.0 (C^{4a}), 147.4 (C^7), 152.0 (C^6), 165.6 (C^1). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 263 (99), $[M - Me]^+$ 248 (100), 220 (26), 206 (97), 178 (61). Found, %: C 68.35; H 8.00; N 5.29. $C_{15}H_{21}NO_3$. Calculated, %: C 68.42; H 8.04; N 5.32.

3,3-Dimethyl-6,7-dipropoxy-3,4-dihydroisoquinolin-1(2*H*)-one (XXg). Yield 1.95 g (67%), mp 137–139°C (EtOH). IR spectrum, cm^{-1}: 3180, 1660, 1606, 1560, 1516. ^1H NMR spectrum, δ, ppm: 1.03 m (6H, 2Me), 1.29 s (6H, 2Me), 1.84 m (4H, $2OCH_2C\underline{H}_2Me$), 2.81 s (2H, CH_2), 3.99 m (4H, $2OCH_2$), 5.65 br.s (1H, NH), 6.61 s ($1H_{arom}$), 7.54 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 10.4 (Me), 22.6 ($OCH_2\underline{C}H_2Me$), 29.0 ($C^3\underline{C}H_3$), 41.4 (C^4), 52.3 (C^3), 70.7 (OCH_2), 70.8 (OCH_2), 112.2 (C^8), 112.5 (C^5), 120.2 (C^{8a}), 131.1 (C^{4a}), 148.0 (C^7), 152.6 (C^6), 165.6 (C^1). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 291 (69), $[M - Me]^+$ 276 (39), 234 (100), 192 (76). Found, %: C 69.98; H 8.73; N 4.78. $C_{17}H_{25}NO_3$. Calculated, %: C 70.07; H 8.65; N 4.81.

6,7-Dibutoxy-3,3-dimethyl-3,4-dihydroisoquinolin-1(2*H*)-one (XXh). Yield 2.97 g (93%), mp 152–153°C (EtOH). IR spectrum, cm^{-1}: 3162, 1660, 1604, 1512. ^1H NMR spectrum, δ, ppm: 0.97 m (6H, 2Me), 1.29 s (6H, 2Me), 1.50 m (4H, $2OCH_2CH_2C\underline{H}_2Me$), 1.80 m (4H, $2OCH_2C\underline{H}_2CH_2CH_3$), 2.81 s (2H, CH_2), 4.00 m (4H, $2OCH_2$), 6.60 s ($1H_{arom}$), 7.54 s ($1H_{arom}$). ^{13}C NMR spectrum, δ, ppm: 13.6 (2C, Me), 18.9 (2C, $OCH_2CH_2\underline{C}H_2Me$), 28.5 ($C^3\underline{C}H_3$), 31.0 ($OCH_2\underline{C}H_2CH_2Me$), 31.1 ($OCH_2\underline{C}H_2CH_2Me$), 41.0 ($C^4$), 51.8 ($C^3$), 68.6 ($OCH_2$), 68.8 ($OCH_2$), 111.8 ($C^8$), 112.2 ($C^5$), 120.2 ($C^{8a}$), 131.0 ($C^{4a}$), 147.6 ($C^7$), 152.3 ($C^6$), 165.6 ($C^1$). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 319 (100), $[M - Me]^+$ 304 (41), $[M - C_4H_9]^+$ 262 (53), 248 (83), 220 (17), 207 (71), 192 (72). Found, %: C 71.56; H 9.08; N 4.42. $C_{19}H_{29}NO_3$. Calculated, %: C 71.44; H 9.15; N 4.38.

1,3,3-Trimethyl-7-methoxy-6-propoxy-3,4-dihydroisoquinoline hydrochloride (XXIa). Yield 1.04 g (35%), mp 183–186°C (ethyl acetate). IR spectrum, cm^{-1}: 1650, 1604, 1565, 1517. ^1H NMR spectrum, δ, ppm: 1.07 t (3H, Me, *J* 7.4 Hz), 1.59 s (6H, 2Me), 1.92 m (2H, $OCH_2C\underline{H}_2Me$), 2.96 s (2H, CH_2), 2.98 s (3H, Me), 3.94 s (3H, OMe), 4.10 t (2H, OCH_2), 6.77 s ($1H_{arom}$), 7.18 s ($1H_{arom}$), 14.37 s (1H, HCl). ^{13}C NMR spectrum, δ, ppm: 10.2 (Me), 19.2 (Me), 22.0 ($OCH_2\underline{C}H_2Me$), 25.8 ($C^3\underline{C}H_3$), 39.3 (C^4), 55.1 (C^3), 56.4 (OMe), 70.9 (OCH_2), 111.4 (C^5), 111.9 (C^8), 116.6 (C^{8a}), 131.8 (C^{4a}), 148.7 (C^6), 156.1 (C^7), 171.9 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 261 $[M - HCl]^+$ (100), 246 $[M - HCl - Me]^+$ (38), 219 (24), 218 (60), 204 (47), 177 (27). Found, %: C 64.61; H 8.08; N 4.64. $C_{16}H_{23}NO_2 \cdot HCl$. Calculated, %: C 64.53; H 8.12; N 4.70.

6-Butoxy-1,3,3-trimethyl-7-methoxy-3,4-dihydrooisoquinoline hydrochloride (XXIb). Yield 0.84 g (27%), mp 187–188°C (toluene). IR spectrum, cm^{-1}: 1596, 1560, 1514. ^1H NMR spectrum, δ, ppm: 1.00 t (3H, Me, *J* 7.4 Hz), 1.51 m (2H, $OCH_2CH_2C\underline{H}_2Me$), 1.59 s (6H, 2Me), 1.89 m (2H, $OCH_2C\underline{H}_2CH_2Me$), 2.94 s (2H, CH_2), 2.96 s (3H, Me), 3.97 q (3H, OMe), 4.13 m (2H, OCH_2), 6.74 s ($1H_{arom}$), 7.14 s ($1H_{arom}$), 14.53 s (1H, HCl). ^{13}C NMR spectrum, δ, ppm: 13.5 (Me), 18.8 ($OCH_2CH_2\underline{C}H_2Me$), 18.9 ($OCH_2CH_2\underline{C}H_2Me$), 19.1 (Me), 25.8 ($C^3\underline{C}H_3$), 30.6 ($OCH_2\underline{C}H_2CH_2Me$), 39.3($C^4$), 55.1 ($C^3$), 56.4 (OMe), 69.1 ($OCH_2$), 111.5 ($C^8$), 111.9 ($C^5$), 116.6 ($C^{8a}$), 131.8 ($C^{4a}$), 148.7 ($C^7$), 156.2 ($C^6$), 171.8 ($C^1$). Mass spectrum, *m/z* (I_{rel}, %): $[M - HCl]^+$ 275 (100), $[M - HCl - Me]^+$ 260 (36), 218 (60), 204 (47), 177 (30). Found, %: C 65.39; H 8.36; N 4.43. $C_{17}H_{25}NO_2 \cdot HCl$. Calculated, %: C 65.48; H 8.40; N 4.49.

6,7-Dibutoxy-1,3,3-trimethyl-3,4-dihydroisoquinoline hydrochloride (XXIc). Yield 1.52 g (43%), mp 180–187°C (ethyl ether). IR spectrum, cm^{-1}: 1636, 1600, 1558, 1516. ^1H NMR spectrum, δ, ppm: 0.99 t (6H, 2Me, *J* 7.4 Hz), 1.51 m (4H, $2OCH_2CH_2C\underline{H}_2Me$), 1.59 s (6H, 2Me), 1.83 m (4H, $2OCH_2C\underline{H}_2CH_2Me$), 2.93 s (3H, Me), 4.01 t (2H, OCH_2, *J* 6.5 Hz), 4.10 t (2H, OCH_2, *J* 6.5 Hz), 6.71 s ($1H_{arom}$), 7.16 s ($1H_{arom}$),

14.49 s (1H, HCl). ^{13}C NMR spectrum, δ, ppm: 13.6 (Me), 18.9 ($OCH_2CH_2\underline{C}H_2Me$), 19.0 (Me), 25.8 ($C^3\underline{C}H_3$), 30.6 ($OCH_2\underline{C}H_2CH_2Me$), 30.9 ($OCH_2\underline{C}H_2CH_2Me$), 39.3 ($C^4$), 55.1 ($C^3$), 69.0 ($OCH_2$), 69.5 ($OCH_2$), 112.2 ($C^5$), 113.5 ($C^8$), 116.5 ($C^{8a}$), 131.8 ($C^{4a}$), 148.3 ($C^6$), 156.8 ($C^7$), 171.7 ($C^1$). Mass spectrum, *m/z* (I_{rel}, %): $[M - HCl]^+$ 317 (100), $[M - HCl - Me]^+$ 302 (79), 275 (32), $[M - HCl - C_4H_9]^+$ 260 (77), 246 (39), 204 (71), 190 (77). Found, %: C 67.95; H 9.10; N 3.88. $C_{20}H_{31}NO_2 \cdot HCl$. Calculated, %: C 67.87; H 9.11; N 3.96.

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REFERENCES

1. Shklyaev Yu.V., Vshivkova T.S., and Tolstikov A.G., *Khim. Geterotsikl. Soedin.,* 2009, p. 421.
2. Brossi A. and Teitel S., *Helv. Chim. Acta,* 1970, vol. 53, p. 1779.
3. Charifson P.S., Wyrick S.D., Hoffmann A.J., Simmons R.M.A., Bowen J.P., McDougald D.L., and Mailman R.B., *J. Med. Chem*., 1988, vol. 31, p. 1941.
4. Chen S., Liu X.-J., Lu Z.-X., Xie Q., and Ling N., *J. Med. Chem.*, 2001, vol. 44, p. 4001.
5. Bindra J.S. and Grodski A., *J. Org. Chem.*, 1977, vol. 42, p. 910.
6. White J.D. and Straus D.S., *J. Org. Chem.,* 1967, vol. 32, p. 2689.
7. Grethe G., Toome V., Lee H.L., Uskokovic M., and Brossi A., *J. Org .Chem*., 1968, vol. 33, p. 504.
8. Shklyaev Yu.V. and Nifontov Yu.V., *Izv. Akad. Nauk, Ser. Khim*., 2002, p. 780.
9. *Obshchii praktikum po organicheskoi khimii* (General Practocum on organic Chemsitry), Kost, A.N., Ed., Moscow: Mir, 1965.