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Dedicated to the Full Member of the Russian Academy of Sciences V.A.Tartakovsky on occasion of his 75th birthday

Chemistry of Naphthazarine Derivatives: XIV.* Preparative Synthesis of 1'-Bromoalkylnaphthazarines

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Abstract—A reaction of alkylnaphthazarines with bromine in tetrachloromethane was investigated. A preparative synthesis was developed for substituted 1'-bromoalkylnaphthazarines, and based on the substance 1'-hydroxyalkylnaphthazarines were prepared, analogs of shikalkin, a racemic mixture of plant pigments from *Boraginaceae* family. 2-Acyl-3-hydroxynaphthazarine was synthesized, a minor metabolite of urchin from genus *Echinothrix.*

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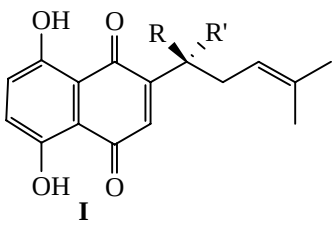
Shikonin (**Ia**), alkanin (**Ib**), and their derivatives, pigments of the plants frm *Boraginaceae* family were subjected to many chemical and biological studies within several last decades [2]. The special attention to this group of compounds is due to their versatile biological action (antimicrobial, antitumor), and also to efficient wound and burn healing properties [3].

In the study of prototropic tautomerism of shikalkin (mixture of epimers **Ia** and **Ib**) and its analogs by means of IR spectroscopy we used as model compounds derivatives of 1'-hydroxyalkylnaphthazarine (5,8-dihydroxy-1,4-naphthoquinone) [4]. These compounds can be easily obtained by nucleophilic substitution of a bromine by an acetoxy function in 1'-bromoalkyl derivatives of naphthazarine followed by hydrolysis of the corresponding 1'-acetoxyalkyl derivatives [5]. Besides the 1'-bromoalkylnaphthazarines are of proper interest as convenient substrates for subsequent functionalization of the side chain. In this connection we performed a detailed study of the bromination of substituted alkylnaphthazarines in nonpolar aprotic medium employing molecular bromine as a brominating agent. We report here on the results of this investigation.



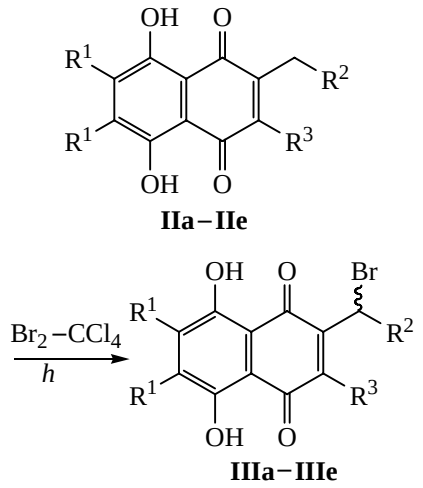
I

R = OH, R' = H (**a**); R = H, R' = OH (**b**).

We found that the bromination of alkylnaphthazarines **IIa–IIe** by excess Br_2 in CCl_4 solution under direct sun light proceeded exclusively at the 1'-position. Therewith compounds **IIIa–IIIe** with a single halogen atom in the side chain were obtained in a good yield (Scheme 1). The reaction time depended on the presence of R^1 and R^3 substituents and varied from 0.5 to 24 h. For instance, ethyl- (**IIa**) and methylnaphthazarines (**IIb**) underwent bromination in these conditions only at sufficiently long exposure of the reaction mixture in the light (12–24 h). At the same time in the presence in the naphthazarine molecule alongside the alkyl group also of other substituents, like Cl, OEt (compounds **IIc–IIe**), the reaction rate grew considerably, and the corresponding bromoalkylnaphthazarines **IIIc–IIIe** formed within 0.5–1 h. The naphthazarine framework and the alkoxy groups were not affected in this case.

* For Communication I, see [1].

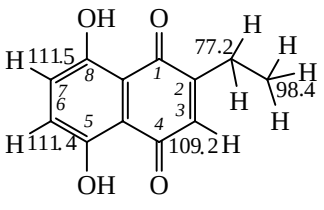
Scheme 1.



$R^1 = R^3 = H$, $R^2 = CH_3$ (**a**); $R^1 = R^2 = R^3 = H$ (**b**); $R^1 = Cl$, $R^2 = CH_3$, $R^3 = H$ (**c**); $R^1 = Cl$, $R^2 = CH_3$, $R^3 = OEt$ (**d**); $R^1 = Cl$, $R^2 = H$, $R^3 = OEt$ (**e**).

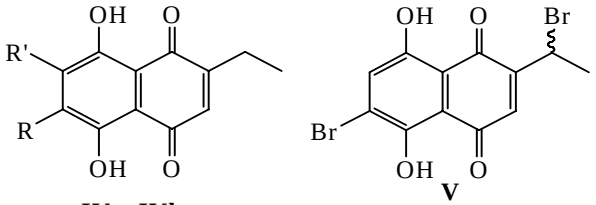
The reaction occurs by the free radical mechanism as confirms the bromination of ethylnaphthazarine (**IIa**) under various conditions. As expected, in the dark and at cooling of the reaction mixture initial naphthazarine **IIa** remained intact. However under the scattered light and at room temperature a regioselective reaction occurred giving 1'-bromoethylnaphthazarine (**IIIa**) in 64% yield. Under bright sun light the yield of compound **IIIa** grew significantly (up to 86%). Another argument confirming the radical reaction mechanism [6] was the formation of 2-bromomethyl derivative **IIIe** at the treatment of substrate **IIe** with *N*-bromosuccinimide in CCl_4 solution under reflux.

The regioselectivity of the radical bromination of alkylnaphthazarines **IIa–IIe** is governed by the relative energy of hemolytic dissociation of various bonds D_0(C–H). Our calculations show (see the figure) that the energy of dissociation of the C$^{1'}$–H bond is smaller by about 21 kcal mol^{-1} than the energy of dissociation of the C$^{2'}$–H bond and by about 32–34 kcal mol^{-1} smaller than the D_0(C–H) values for the C–H bonds of the naphthazarine skeleton.



Energy of dissociation of bonds D_0(C–H), kcal mol^{-1}, of ethylnaphthazarine (**IIa**), calculated by UB3LYP/6-311G(d) method.

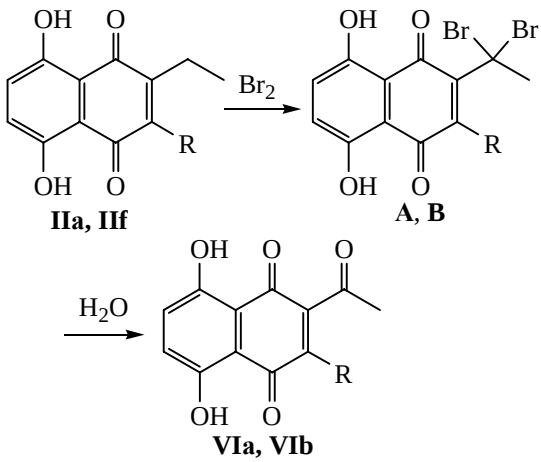
At the use of a polar protonic solvent (acetic acid) the bromination of ethylnaphthazarine (**IIa**) proceeded only at heating, the main reaction product was also bromoethylnaphthazarine **IIIa** but in lower yield (50%). Beside compound **IIIa** we isolated from the reaction mixture products of heterolytic bromination in the ring (**IVa** and **IVb**), and compound **V** resulting from a simultaneous halogenation both in the ring and the side chain.



R = Br, R' = H (**a**), R = H, R' = Br (**b**).

The presence in the naphthazarine structure of a free β-hydroxy group in the *ortho*-position to the alkyl substituent resulted in the formation on bromination of complex products mixtures which we failed to separate. Of certain interest was the bromination of 2-alkyl-3-hydroxynaphthazarine **IIf**. As a result of this reaction and of the subsequent treatment of the reaction mixture we obtained in ~19% yield acetylhydroxynaphthazarine (**VIb**), one of metabolites of urchin from genus *Echinothrix* [7] (Scheme 2). Compound **VIb** is presumably a hydrolysis product of the primary forming in the

Scheme 2.



II, R = H (**a**), OH (**f**); **VI**, R = H (**a**), OH (**b**); R = H (**A**), OH (**B**).

course of reaction *gem*-dibromide **B**. Acetylhydroxynaphthazarine (**VIb**) was isolated as an impurity (0.05%) at reduction of 3-acetyl-2,7-dihydroxynaphthazarine (spinochrome A) with sodium borohydride [18]. A former purposive synthesis [9] was multistage, and the initial compound, trimethyl ether of 2,5,8-trihydroxy-1,4-naphthoquinone, was difficultly aavailable. The method we have developed for preparation of naphthazarine **VIb** is the first one-stage synthesis of this natural compound providing a fair yield.

The bromination of ethylnaphthazarine (**IIa**) also yielded acetyl derivative **VIa** as minor product. The formation of compounds of **VIa** and **VIb** type suggests the facility of hydrolysis of the arising intermediate dibromo derivatives **A** and **B,** and the low yields of compounds **VIa** and **VIb** are caused by the negative inductive effect of the bromine atom reducing the rate of the second bromination step.

As already mentioned 1'-bromoalkylnaphthazarines **IIIa** and **IIIb** are easily converted into the corresponding 1´-hydroxyalkylnaphthazarines **VIIIa** and **VIIIb**. Compounds **IIIa** and **IIIb** when treated with sodium acetate readily yield acetoxy derivatives **VIIa** and **VIIb** which on hydrolysis effected by trifluoroacetic acid provided naphthoquinones **VIIIa** and **VIIIb** as a racemic mixture of epimers (1'-*R*) and (1'-*S*) modeling shikalkin (**I**) (Scheme 3).

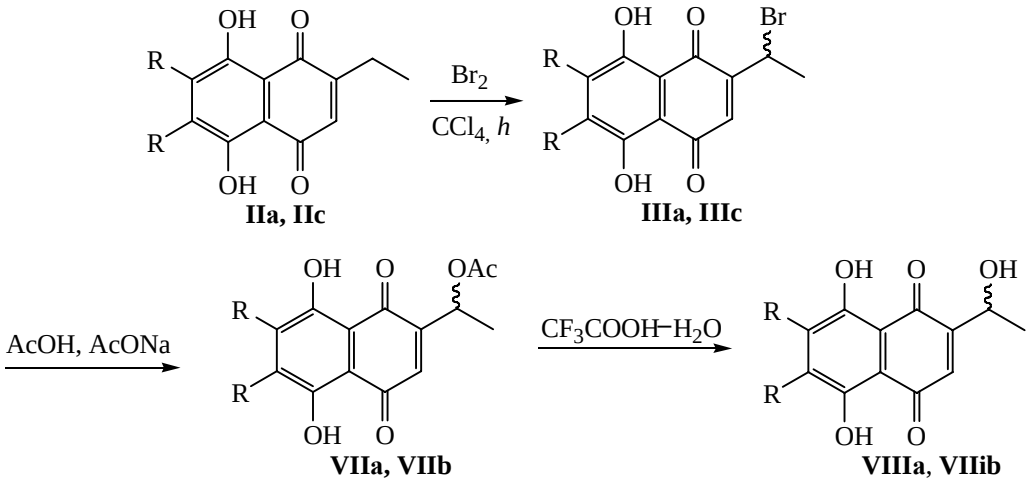
Dichloronaphthazarines are known to undergo easily a reductive dehalogenation [10], but we have not succeeded in converting dichloride **IIIc** into compound **IIIa**. From the complex reaction mixture a product of bromine replacement by a hydroxy group **VIIIb** was isolated in a low yield, but the desired dehalogenation product **IIIa** was not detected even in traces.

Thus alkylnaphthazarines **IIa–IIe** obey to the classical rules of aromatic compounds halogenation. The nonpolar medium favors bromination into the α-position of alkyl group attached to deactivated aromatic system. A simple and efficient preparative method was developed for the synthesis of substituted 1'-bromoethylnaphth-azarine, initial substrates for subsequent functionalization of substituted naphthazarines.

EXPERIMENTAL

The melting points has been measured on a Bo¸tius heating block and are reported uncorrected. IR spectra were recorded on a spectrophotometer Bruker Vector-22 from solutions in $CHCl_3$. ^1H NMR spectra were registered on a spectrometer Bruker AC-250 (250.13 MHz) in $CDCl_3$ (internal reference Me_4Si). Mass spectra (electron impact) were measured on LKB-9000S instrument with a direct sample admission at the ionizing electrons energy 70 eV. The monitoring of the reactions progress and checking the homogeneity of compounds obtained was performed by TLC on Sorbfil plates, eluent hexane–acetone, 2:1. Elemental analysis was carried out on a CHN-analyzer Flash EA-1112 (Institute of Chemistry and Applied Ecology at the Far-Eastern State University, Vladivostok). The yields of compounds obtained were

Scheme 3.



II, III, R = H (**a**), Cl (**c**); **VII, VIII**, R = H (**a**), Cl (**b**).

not optimized. The synthesis of initial compounds **IIa** and **IIc** [11], **IId** and **IIe** [12], and **IIf** [13] was performed using known procedures. Compound **IIb** was synthesized by reductive dehalogenation of 5,8-dihydroxy-2-methyl-6,7-dichloro-1,4-naphthoquinone [10]. Synthesis of compounds **VIIa** and **VIIIa** was described in [4]. The optimization of geometry and the calculation of the frequencies of normal vibrations for ethylnaphthazarine (**IIa**) and its radicals was performed by the method (U)B3LYP/6-311G(d) with exchange-correlation functional B3LYP [14] using software package PC GAMESS [15]. Energy of dissociation D_o(X–H) of a bond X–H was calculated by a formula: $D_o(X–H) = E(X^·) + E_o(H^·) + (3/2)RT – E(X–H)$ where $E = E_o + ZPE$, E_o and ZPE are respectively the energy of the ground electronic state and the energy of the zero vibrations; $E_o(H^·)$ is the energy of the ground electronic state of a hydrogen atom equal –0.502156 a.u.; $(3/2)RT$ is the translatory energy of a hydrogen atom equal 0.889 kcal mol^{-1} at 298.15 K.

Bromination of alkylnaphthazarines IIa–IIf with molecular bromine in CCl_4. General procedure. To a solution of 0.2 mmol of naphthazarine in 50 ml of CCl_4 was added at room temperature 10 μl of Br_2, and the reaction mixture was kept in light within 0.5 – 24 h. On completion of the reaction the solvent was removed under a vacuum, the residue was subjected to preparative TLC (eluent hexane–acetone, 3:1), or it was recrystallized from ethanol.

2-(1'-Bromoethyl)-5,8-dihydroxy-1,4-naphthoquinone (IIIa). Yield 86%, dark-red crystals, mp 127–137°C (127–137°C [4]). IR spectrum, ν, cm^{-1}: 3050, 1659, 1613, 1571. ^{1}H NMR spectrum, δ, ppm: 1.99 d (3H, CH_3, *J* 6.8 Hz), 5.47 q.d (1H, H$^{1'}$, J_1 6.8, J_2 0.7 Hz), 7.20 s (2H, H^6, H^7), 7.28 d (1H, H^3, *J* 0.7 Hz), 12.40 s, 12.64 s (2H, α-OH). Mass spectrum, *m/z* (I_{rel}, %): 296/298 [*M*]$^+$ (19), 219 [*M* – Br]$^+$ (100).

2-Bromomethyl-5,8-dihydroxy-1,4-naphthoquinone (IIIb). Yield 40%, dark-red crystals, mp 130–135°C. ^{1}H NMR spectrum, δ, ppm: 4.45 C (2H, CH_2Br), 7.19 C (1H, H^3), 7.21 d, 7.24 d (2H, H^6 and H^7, *J* 9.7 Hz), 12.38 s, 12.59 s (2H, α-OH). Mass spectrum, *m/z* (I_{rel}, %): 282/284 [*M* + 1]$^+$ (96), 281/283 [*M*]$^+$ (84), 204 (100), 203 (89). Found, %: C 46.48; H 2.64. $C_{11}H_7BrO_4$. Calculated, %: C 46.67; H 2.49.

2-(1'-Bromoethyl)-5,8-dihydroxy-6,7-dichloro-1,4-naphthoquinone (**IIIc**). Yield 70%, golden-brown crystals, mp 210–213°C (acetone). IR spectrum, ν, cm^{-1}: 2980, 1928, 1624 (C=O), 1576, 1564 (C=C). ^{1}H NMR spectrum, δ, ppm: 2.03 d (3H, CH_3, *J* 7.1 Hz), 5.55 q (1H, H$^{1'}$, *J* 7.1 Hz), 7.52 s (1H, H^3), 12.34 s, 12.94 s (2H, α-OH). Mass spectrum, *m/z* (I_{rel}, %): 364/366/368/370 [*M*]$^+$ (27), 363/365/367/369 [*M* – 1]$^+$ (30), 285/287/289 [*M* – Br]$^+$ (100), 284/286/288 [*M* – Br – H]$^+$ (99), 256/258/260 (21), 255/257/259 (18). Found, %: C 39.68; H 2.02. $C_{12}H_7BrCl_2O_4$. Calculated, %: C 39.38; H 1.93.

2-(1'-Bromoethyl)-5,8-dihydroxy-6,7-dichloro-3-ethoxy-1,4-naphthoquinone (**IIId**). Yield 76%, red crystals, mp 142–144°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 1.54 t (3H, CH_3, *J* 7.1 Hz), 2.07 d (3H, CH_3, *J* 7.1 Hz), 4.63 q (2H, CH_2, *J* 7.1 Hz), 5.66 q (1H, CHBr, *J* 7.1 Hz), 12.84 s, 13.41 s (2H, α-OH). Mass spectrum, *m/z* (I_{rel}, %): 408/410/412/414 [*M*]$^+$ (14), 329/331 (82), 330/332 [*M* – Br]$^+$ (100), 328 (60), 327 (47), 301 (38). Found, %: C 41.03; H 2.75. $C_{14}H_{11}BrCl_2O_5$. Calculated, %: C 41.01; H 2.70.

2-Bromomethyl-5,8-dihydroxy-6,7-dichloro-3-ethoxy-1,4-naphthoquinone (**IIIe**). Yield 76%, red crystals, mp 179–180°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 1.51 t (3H, CH_3, *J* 7.1 Hz), 4.50 s (2H, CH_2Br), 4.70 q (2H, CH_2, *J* 7.1 Hz), 12.85 s, 13.27 s (2H, α-OH). Mass spectrum, *m/z* (I_{rel}, %): 394/396/398/400 [*M*]$^+$ (15), 393/395/397/399 [*M* – 1]$^+$ (15), 316/318/320 [*M* – Br]$^+$ (100). Found, %: C 39.30; H 2.38. $C_{13}H_9BrCl_2O_5$. Calculated, %: C 39.43; H 2.29.

6-Bromo-2-(1'-bromoethyl)-5,8-dihydroxy-1,4-naphthoquinone (V). Yield 24 mg (13%), dark-red crystals, mp 105–110°C. ^{1}H NMR spectrum, δ, ppm: 2.01 d (3H, CH_3, *J* 6.8 Hz), 5.49 q (1H, H$^{1'}$, *J* 6.8 Hz), 7.59 s (1H, H^7), 7.36 s (1H, H^3), 12.58 s, 12.68 s (2H, α-OH). Mass spectrum, *m/z* (I_{rel}, %): 374/376/378 [*M*]$^+$ (7), 295/297 (57), 294/296 (70), 217 (43). Found, %: C 38.30; H 2.20. $C_{12}H_8Br_2O_4$. Calculated, %: C 38.33; H 2.14.

2-Acetyl-5,8-dihydroxy-1,4-naphthoquinone (**VIa**). Yield 1%, red crystals, mp 130°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 2.72 s (3H, CH_3), 7.10 d (1H, H^6, *J* 10 Hz), 7.13 d (1H, H^7, *J* 10 Hz), 7.63 s (1H, H^3), 12.16 s, 13.10 s (2H, α-OH). Mass spectrum, *m/z* (I_{rel}, %): 232 [*M*]$^+$ (100), 218 (41), 217 (93), 189 (36).

2-Acetyl-3,5,8-trihydroxy-1,4-naphthoquinone (**VIb**). Yield 19%, red crystals, mp 146–148°C {163–164°C (decomp.) [9]}. ^{1}H NMR spectrum, δ, ppm: 2.88 s (3H, CH_3), 7.28 d (1H, H_{arom}, *J* 9.5 Hz), 7.38 d (1H, H_{arom}, *J* 9.5 Hz), 12.25 s, 13.04 s (2H, α-OH). Mass spectrum, *m/z* (I_{rel}, %): 249 [*M* + 1]$^+$ (30), 248 [*M*]$^+$ (100), 220 (28), 206 (33), 205 (100), 178 (56).

Bromination of alkylnaphthazarine IIe with N-bromosuccinimide. A solution of 72 mg (0.22 mmol)

of compound **IIe**, 80 mg (0.36 mmol) of N-bromosuccinimide, and 2 mg of AIBN in 12 ml of CCl_4 was boiled for 2 h, the solvent was removed, and the residue was crystallized from ethanol to give 72 mg (83%) of compound **IIIe**.

Bromination of ethylnaphthazarine (IIa) with molecular bromine in acetic acid. In 29 ml of acetic acid was dissolved 112 mg of substrate, the solution was heated to 65°C, then 60 μl of Br_2 in 3 ml of acetic acid was added dropwise, and the stirring was continued for 3 h. The reaction mixture was dilutd with water, extracted with ethyl acetate, the extract was dried with anhydrous Na_2SO_4, and evaporated under a vacuum. The products obtained were isolated by column and repeated preparative chromatography using benzene and hexane–acetone as eluents. Yield of compound **IIIa** 47%.

6-Bromo-5,8-dihydroxy-2-ethyl-1,4-naphthoquinone (IVa). Yield 18 mg (13%), dark-red crystals, mp 150–155°C. ^{1}H NMR spectrum, δ, ppm: 1.24 t (3H, CH_3, *J* 7.5 Hz), 2.64 q (2H, CH_2, *J* 7.5 Hz), 6.92 s (1H, H^3), 7.56 s (1H, H^7), 12.56 s, 12.89 s (2H, α-OH). Mass spectrum, *m/z* (I_{rel}, %): 295/297 $[M]^+$ (100), 253/255 (12), 218 (19), 217 (8), 188 (49). Found, %: C 48.49; H 3.10. $C_{12}H_9BrO_4$. Calculated, %: C 48.51; H 3.05.

7-Bromo-5,8-dihydroxy-2-ethyl-1,4-naphthoquinone (IVb). Yield 1.8 mg (1.3%), dark-red crystals. ^{1}H NMR spectrum, δ, ppm: 1.24 t (3H, CH_3, *J* 7.5 Hz), 2.64 q (2H, CH_2, *J* 7.5 Hz), 6.92 s (1H, H^3), 7.59 s (1H, H^7), 12.37 s, 13.06 s (2H, α-OH).

2-(1'-Acetoxyethyl)-5,8-dihydroxy-6,7-dichloro-1,4-naphthoquinone (VIIb). A mixture of 290 mg (0.8 mmol) of compound **IIIc** and 330 mg (4.0 mmol) of AcONa in 12 ml of a mixed solvent AcOH–$CHCI_3$, 3:1, was boiled for 2 h. The solvents mixture was evaporated at a reduced pressure, the residue was diluted with 50 ml of water, extracted with ethyl acetate, the extract was dried with Na_2SO_4, and evaporated at a reduced pressure. By means of column chromatography (eluent benzene) we isolated 224 mg (82%) of the main reaction product **VIIb**. Dark-red crystals, mp 122–124°C (EtOH). IR spectrum, ν, cm^{-1}: 2989, 2937, 2874, 2855, 1754 (OAc), 1625 (C=O), 1578, 1564 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.55 d (3H, CH_3, *J* 6.6 Hz), 2.16 s (3H, OCH_3), 6.16 q (1H, H$^{1'}$, *J* 6.6 Hz), 7.31 s (1H, H^7), 12.38 s, 12.76 s (2H, α-OH). Mass spectrum, *m/z* (I_{rel}, %): 345/347/349 $[M + 1]^+$ (15), 344/346/348 $[M]^+$ (38), 302/304/306 (21), 301/303/305 (20), 285/287/289 (100), 284/286/288 (84), 257/259/261 (24). Found, %: C 48.42; H 2.90. $C_{14}H_{10}Cl_2O_6$. Calculated, %: C 48.47; H 2.92.

5,8-Dihydroxy-2-(1'-hydroxyethyl)-6,7-dichloro-1,4-naphthoquinone (**VIIIb)**. A dispersion of 138 mg (0.4 mmol) of compound **VIIb** in 5 ml of a mixture TFA–H_2O, 2:1, was boiled for 30 min. The solvents mixture was evaporated at a reduced pressure, the residue was dissolved in 50 ml of water. The reaction mixture extracted with ethyl acetate, the extract was dried with Na_2SO_4, and evaporated at a reduced pressure. By means of column chromatography (eluent benzene–acetone, 50:1) we isolated 103 mg (86%) of the main reaction product **VIIIb**. Red-brown crystals, mp 162–163°C. IR spectrum, ν, cm^{-1}: 3614 (C$^{1'}$OH), 2978, 2933, 1619 (C=O), 1573, 1563 (C=C). ^{1}H NMR spectrum, δ, ppm: 1.55 d (3H, CH_3, *J* 6.3 Hz), 5.19 q (1H, H$^{1'}$, *J* 6.3 Hz), 7.45 s (1H, H^7), 12.45 s, 12.86 s (2H, α-OH). Mass spectrum, *m/z* (I_{rel}, %): 303/305/307 $[M + 1]^+$ (25), 302/304/306 $[M]^+$ (100), 287/289/291 (27), 284/286/288 (77), 268/270 (21). Found, %: C 47.0; H 2.74. $C_{12}H_8Cl_2O_5$. Calculated, %: C 47.55; H 2.66.

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