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Amination of 2-Hydroxy- and 2,3-Dihydroxynaphthazarins. Synthesis of Echinamines A and B, Metabolites Produced by the Sand Dollar *Scaphechinus mirabilis*

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Abstract—2-Hydroxynaphthazarins reacted with aqueous ammonia at the C^1=O carbonyl group, following the addition–elimination pattern with formation of 8-aminojuglone derivatives. Reactions of 2,3-dihydroxynaphthazarins with the same reagent involved the C^2=O carbonyl group of the corresponding 1,2-naphthoquinoid tautomer to produce 2-aminonaphthazarin derivatives. 7-Ethyl-2,3,6-trihydroxynaphthazarin (echinochrome) reacted with aqueous ammonia to give 3(2)-amino-7-ethyl-2(3),6-dihydroxynaphthazarins (echinamines A and B) that are metabolites recently isolated from the sand dollar *Scaphechinus mirabilis*.

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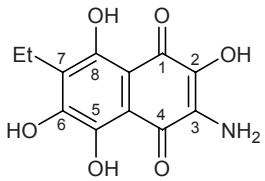
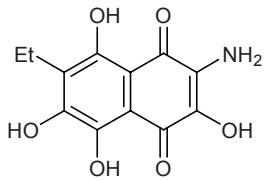
Unlike hydroxy derivatives of naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) [1], the chemistry of its amino-substituted analogs was studied very poorly. On the other hand, isolation of echinamines A (**I**) and B (**II**) (first representatives of hydroxylated naphthazarins having an amino group on the naphthalene ring; hereinafter, only one of all possible tautomers is shown, unless otherwise stated) as metabolites produced by the sand dollar *Scaphechinus mirabilis* has recently been reported. Aminohydroxynaphthazarins **I** and **II** showed a high antioxidant activity *in vitro* [2]. Therefore, search for synthetic approaches to amino-substituted naphthazarins becomes important from both theoretical and practical viewpoints.



I



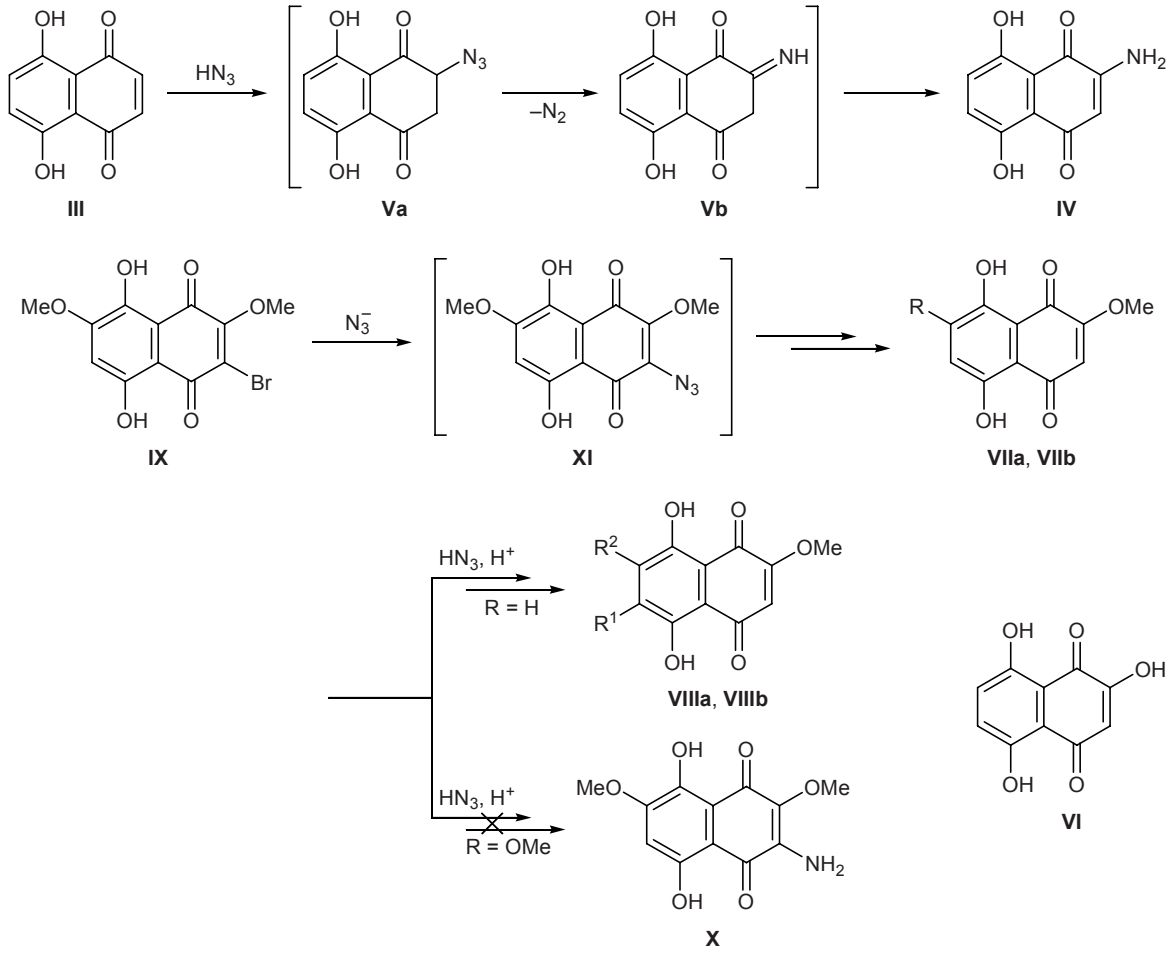
II

A known procedure for the introduction of an amino group into position *2* of naphthazarin (**III**) is based on addition of hydrazoic acid (Scheme 1). Aminonaphthazarin **IV** is the final product of transformation of the primary adduct (**Va**→**Vb**) [3]. This reaction has serious limitations. In our experiments neither hydroxynaphthazarin **VI** nor mompain dimethyl ether **VIIa** took up HN_3, while in the reaction with naphthopurpurin monomethyl ether **VIIb** the addition occurred at the hydroxy-substituted ring to give isomer mixture **VIIIa**/**VIIIb** [4].

A more effective approach involves introduction of an amino group via nucleophilic replacement of halogen by azide ion. An example of such transformation (**IX**→**X**) is shown in Scheme 1. Compound **X** is formed as a result of reduction of the C^2=C^3 double bond in intermediate azidoquinone **XI** with hydrazoic acid liberated upon treatment of the reaction mixture with water [4, 5].

We previously found [6] that the reaction of hydroxynaphthazarins **XII** with aqueous ammonia is strictly regioselective: the products are the corresponding imino derivatives **XIII**. In continuation of these studies we examined reactions of 2-hydroxynaphthazarins **XIVa** and **XIVb** and 2,3-dihydroxynaphthazarins **XVa** and **XVb** with 25% aqueous ammonia. Treatment of hydroxynaphthazarins **XIVa** and **XIVb** with 25% aqueous ammonia at room temperature gave in each case only one (according to the NMR data) naphthazarin derivative having an amino group but

Scheme 1.

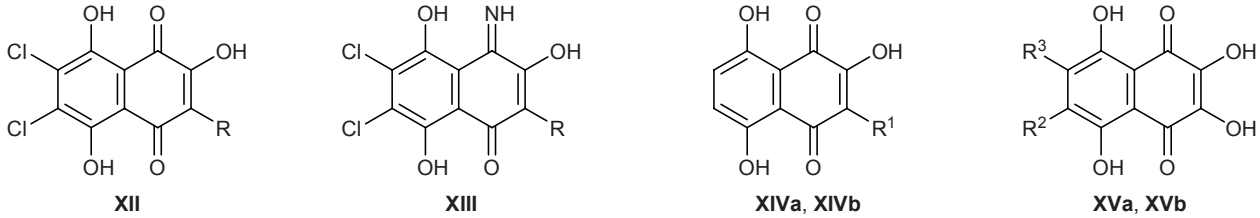


VII, R = OMe (**a**), R = H (**b**); **VIII**, $R^1 = NH_2$, R^2 = H (**a**), R^1 = H, $R^2 = NH_2$ (**b**).

lacking one *peri*-hydroxy group. Taking into account our previous data [6], we presumed that this reaction involves intermediate formation of imino derivatives **XVIa** and **XVIb** which undergo tautomerization into 8-aminojuglones **XVIIa** and **XVIIb** (Scheme 2).

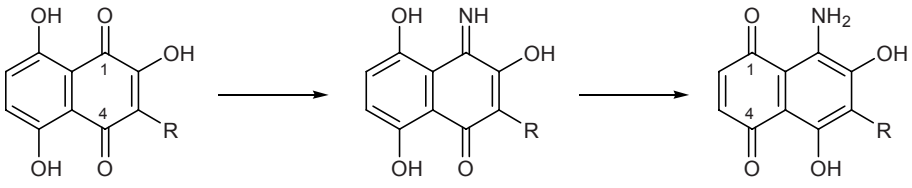
Optimization of the molecular geometry in terms of the density functional theory at the B3LYP/6-31G(*d*) level showed that aminojuglones **XVIIa** and **XVIIb** are characterized by the minimal total energy E_{tot} ($E_{tot} = E_0 + ZPE$, where E_0 is the energy of the ground electronic state, and *ZPE* is the zero-point vibration energy) among all possible tautomers and that quinone imine structures **XVIa** and **XVIb** are unfavorable from the viewpoint of energy. According to the calculations, the differences in the total energies were 5.49 and 4.78 kcal/mol for structures **XVIIa**/**XVIa** and **XVIIb**/**XVIb**, respectively.

The position of the amino group in molecule **XVIIb** was directly proved by the formation of naphtho[1,2-*d*]oxazole **XVIII** in the acid-catalyzed re-



XIV, R^1 = H (**a**), Et (**b**); **XV**, R^2 = Me, R^3 = H (**a**), R^2 = OH, R^3 = Et (**b**).

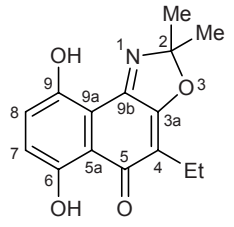
Scheme 2.



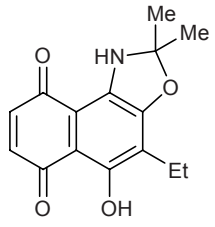
XIVa, **XIVb** **XVIa**, **XVIb** **XVIIa**, **XVIIb**

R = H (**a**), Et (**b**).

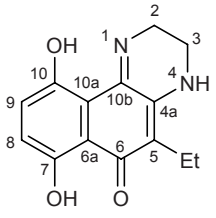
action with acetone and of benzo[*f*]quinoxaline **XIX** in the reaction with of hydroxynaphthazarin **XIVb** with a solution of ethane-1,2,-diamine. Compounds **XVIII** and **XIX** in solution can exist as tautomer couples **XVIIIa**/**XVIIIb** and **XIXa**/**XIXb**. According to the ^{1}H and ^{13}C HMBC NMR data, compound **XVIII** in $CDCl_3$ has the structure of naphtho[1,2-*d*]oxazolone **XVIIIa**, in keeping with the results of calculations by the B3LYP/6-31G(*d*) method. The ^{13}C NMR spectrum of this compound contained only one signal assignable to a carbonyl carbon atom (δ_C 190.3 ppm). The energy of imino tautomer **XVIIIa** is lower by 4.82 kcal/mol than the energy of amino tautomer **XVIIIb**. Assessment of the state of tautomeric equilibrium between **XVIIIa** and **XVIIIb** by the total Gibbs energies gave a ratio of 1000 : 1 for the gas phase.



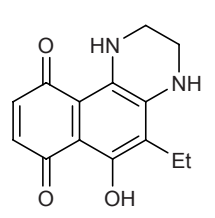
XVIIIa



XVIIIb



XIXa



XIXb

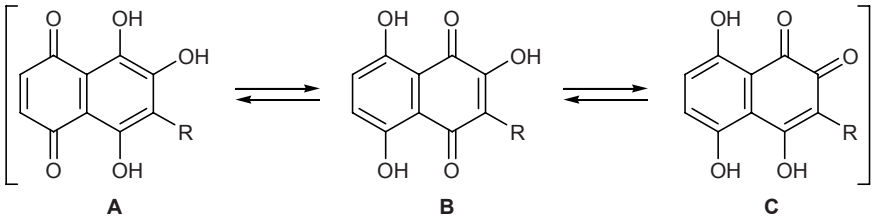
Analysis of the two-dimensional ^{13}C and ^{1}H NMR spectra showed that compound **XIX** in DMSO exists mainly as benzo[*f*]quinoxalinone **XIXa**. Unfortunately, we failed to obtain satisfactory ^{13}C NMR data for a solution of this compound in $CDCl_3$ because of its poor solubility. Like compound **XVIII**, the ^{13}C NMR spectrum of **XIX** contained only one carbonyl carbon signal (δ_C 178.9 ppm), and one NH signal was present in the ^{1}H NMR spectrum (δ 7.66 ppm).

The total energy [B3LYP/6-31G(*d*)] of benzo[*f*]-quinoxalinedione **XIXb** was smaller by 1.89 kcal/mol than that of tautomer **XIXa**; i.e., tautomer **XIXb** should predominate in the gas phase. Estimation of the energy of the transformation **XIXa**↔**XIXb** in terms of the Moeller–Plesset second-order perturbation theory with the same basis set [MP2/6-31G(*d*)] gave ΔE = E(**XIXa**) – E(**XIXb**) = 0.4 kcal/mol, and the concentration ratio **XIXa**/**XIXb** was estimated at 36 : 64. On the other hand, the results of calculation of relative ^{1}H and ^{13}C chemical shifts $\delta_{XY}(^1H) = \delta_X(^1H) - \delta_Y(^1H)$ and $\delta_{XY}(^{13}C) = \delta_X(^{13}C) - \delta_Y(^{13}C)$ (where X and Y are different ^{1}H or ^{13}C nuclei in molecule **XIX**) were consistent only with structure **XIXa**.

Compounds **XIVa** and **XIVb** in solution can exist as two 1,4-naphthoquinoid tautomers **A** and **B** (Scheme 3), so that an amino group could enter position *1*, *4*, *5*, or *8*. However, the observed complete regioselectivity is likely to result from the fact that only 1,2-tautomer **C** is involved in the reaction. In this case, the C^2=O carbonyl group activates the C^1=O group, and the process follows the addition–elimination pattern [7]. Thus the hydroxy group in the 2-position formalistically acts as orienting group in the reaction of monohydroxynaphthazarins with concentrated aqueous ammonia.

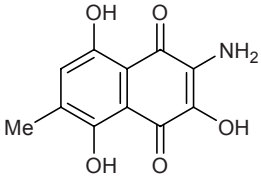
Like monohydroxynaphthazarins **XIVa** and **XIVb**, 2,3-dihydroxynaphthazarin **XVa** reacted with 25% aqueous ammonia to give a chromatographically homogeneous (TLC) product in high yield. However, the ^{1}H NMR data showed that the product was a mixture of two compounds at a ratio of 1 : 1.5. We failed to separate this mixture by other chromatographic methods, including HPLC. According to the ^{1}H NMR spectrum, the naphthazarin system was conserved in their molecules. The spectrum contained signals typical of protons in α-hydroxy groups at δ 11.64, 11.75 and 11.22, 12.08 ppm, respectively. In addition, signals

Scheme 3.

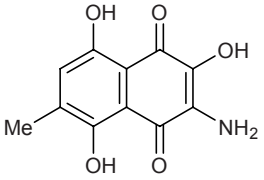


XIVa, **XIVb**

typical of amino group on C^2 or C^3 were present at δ 5.35 and 5.12 ppm with the same intensity ratio [4]. Taking into account the other signals (see Experimental), the products were assigned the structures of 2-amino-3-hydroxy-6-methylnaphthazarin (**XX**) and 3-amino-2-hydroxy-6-methylnaphthazarin (**XXI**). Thus the presence of two neighboring β-hydroxy groups in the naphthazarin system forwards the reaction with ammonia to position *2* or *3*.



XX

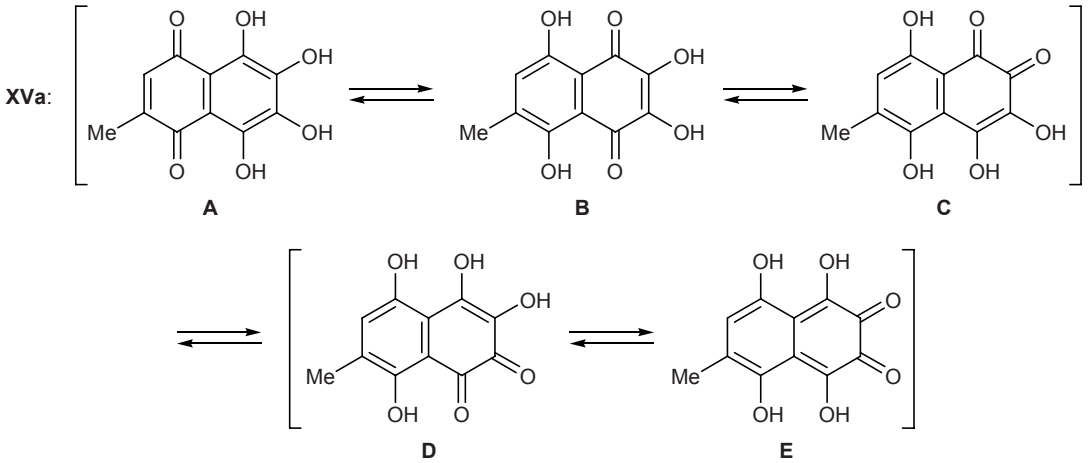


XXI

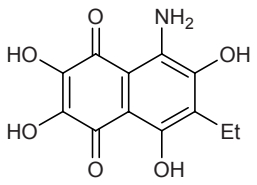
Obviously, apart from 1,4-naphthoquinoid tautomers **A** and **B**, 2,3-dihydroxynaphthazarin (**XVa**) could give rise to several 1,2-naphthoquinoid tautomers, such as **C**, **D**, and **E** (Scheme 4; for the sake of simplicity, anionic forms are not considered, though compound **XVa** reacts just in the anionic form). On the basis of the obtained results and generally accepted views on the reactivity of structurally related compounds, we presumed that just tautomers **C**, **D**, and **E** (especially the latter) are responsible for the observed regioselectivity in the amination of compound **XVa**. Quantum-chemical simulation of the behavior of the compounds under study in basic medium fall beyond the scope of the present work, and detailed mechanism of the above reaction still remains an open question.

Echinochrome molecule **XVb*** includes fragments of 3-ethyl-2-hydroxy- and 2,3-dihydroxynaphthazarins **XIVb** and **XVa**. It might be expected that echinochrome **XVb** should react with aqueous ammonia to afford a mixture of 8-aminojuglone (**XXII**) and 3(2)-aminonaphthazarins **I** and **II**. However, we found that this reaction leads to the formation of a mixture of 3-amino-2,6-dihydroxy- and 2-amino-3,6-dihydroxy-7-ethylnaphthazarins **I** and **II** in nearly quantitative overall yield. We succeeded in separating the product mixture by chromatography, and each component was fully characterized by spectral and analytical data. The prod-

Scheme 4.



* Specificity of spin density distribution and geometric parameters of different rotamers and tautomers of echinochrome A, its anions, radicals, and radical anions were considered in [8].



XXII

ucts turned out to be identical to echinamines **A** and **B** that are first nitrogen-containing hydroxynaphthazarins isolated recently from the sand dollar *S. mirabilis* [2].

Thus 2-hydroxynaphthazarins react with aqueous ammonia at the C^1=O carbonyl group according to the addition–elimination pattern to produce in the general case mixtures of tautomeric 1,4-naphthoquinone 1-imines and 8-aminojuglone derivatives. The reaction of 2,3-dihydroxynaphthazarins with aqueous ammonia involves the C^2=O and C^3=O carbonyl groups in the corresponding 2,3-naphthoquinone tautomers, and the products are mixtures of 2 and 3-aminonaphthazarins.

EXPERIMENTAL

The melting points were determined on a Boetius melting point apparatus and are uncorrected. The IR spectra were recorded from solutions in $CDCl_3$ on a Bruker Vector 22 spectrometer with Fourier transform. The NMR spectra were measured on Bruker Avance DPX-300 and DRX-500 spectrometers relative to tetramethylsilane as internal reference; in the spectra recorded from solutions in DMSO-d_6, the chemical shifts were measured relative to the solvent signals (δ 2.5 ppm, δ_C 39.6 ppm). Two-dimensional HMBC experiments were performed according to standard procedure at room temperature with optimization for long-range coupling constants of 2.5 and 10.0 Hz. The mass spectra (electron impact, 70 eV) were obtained on an LKB-9000S instrument with direct sample admission into the ion source. The high-resolution mass spectra (electron impact, 70 eV) were recorded on an AMD-604S mass spectrometer. The elemental compositions were determined on a Flash EA-1112 CHN analyzer at the Institute of Chemistry and Applied Ecology (Far East State University, Vladivostok, Russia). The progress of reactions and the purity of products were monitored by TLC on Merck 60F-254 plates. Individual compounds were isolated from product mixtures by preparative thin-layer chromatography on silica gel plates (H^+-form, unfixed layer, 5–40 μm) [9]. Echinamines **A** and **B** were separated by column chromatography on TSK gel Toyopearl HW-40 using 40% ethanol containing 0.6% of HCOOH as eluent. The yields were not optimized.

Initial 2-hydroxynaphthazarins **XIVa** [10] and **XIVb** [11] and 2,3-dihydroxynaphthazarins **XVa** [12] and **XVb** [13] were synthesized according to known methods. Quantum-chemical calculations were performed in terms of the density functional theory using B3LYP exchange correlation functional and of the Moeller–Plesset second-order perturbation theory (MP2). The electronic energies E_0 and corrections for zero-point vibration energy (*ZPE*) were calculated by full geometry optimization using 6-31G(*d*) basis set. The Gibbs energies *G* were calculated with account taken of all electronic, translational, rotational, and vibrational degrees of freedom at 298.15 K. The magnetic shielding constants were determined by the B3LYP/6-31G(*d*)-GIAO and PBE/3z-GIAO methods for structures optimized at the B3LYP/6-31G(*d*) level. All B3LYP/6-31G(*d*) calculations were performed using Gaussian G03W [14] and PC GAMESS software packages [15], and PBE/3z-GIAO calculations were performed using PRIRODA software [16].

Aminohydroxynaphthoquinones (*general procedure***).** The corresponding hydroxynaphthazarin, 0.39 mmol, was dissolved in 10 ml of ethanol, 5 ml (83 mmol) of 25% aqueous ammonia was added under stirring, and the mixture was stirred at room temperature until the reaction was complete according to the TLC data. The mixture was then kept for 30 min under reduced pressure (~20 mm, bath temperature 50°C) to remove excess ammonia, cooled, and acidified to pH 3 with 5% hydrochloric acid.

In the synthesis of compounds **XVIIa** and **XVIIb** from 2-hydroxynaphthazarins **XIVa** and **XIVb**, the reaction time was 5 min. After acidification, a finely crystalline material separated and was filtered off, washed with water (3×3 ml), and dried under reduced pressure over NaOH.

8-Amino-5,7-dihydroxy-1,4-dihydronaphthalene-1,4-dione (XVIIa). Yield 94%, violet powder, mp 190°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 6.39 s (1H, 6-H), 6.92 d (1H, 3-H, J = 10.2 Hz), 7.01 d (1H, 2-H, J = 10.2 Hz), 8.84 br.s (2H, NH_2), 11.13 br.s (1H, β-OH), 14.98 br.s (1H, α-OH). Mass spectrum, m/z (I_{rel}, %): 206 $[M + 1]^+$ (100), 205 $[M]^+$ (57), 150 (32), 149 (49), 126 (47), 124 (38), 61 (33), 57 (44), 33 (72). Found, %: C 58.46; H 3.50; N 6.91. $C_{10}H_7NO_4$. Calculated, %: C 58.54; H 3.44; N 6.83.

8-Amino-6-ethyl-5,7-dihydroxy-1,4-dihydronaphthalene-1,4-dione (XVIIb). Yield 86%, violet powder, mp 250°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.05 t (3H, CH_3, J = 7.3 Hz),

2.64 q (2H, CH_2, J = 7.3 Hz), 6.90 d (1H, 3-H, J = 10.1 Hz), 7.03 d (1H, 2-H, J = 10.1 Hz), 9.16 br.s (2H, NH_2), 11.16 br.s (1H, β-OH), 15.57 br.s (1H, α-OH). Mass spectrum, m/z (I_{rel}, %): 234 $[M + 1]^+$ (85), 233 $[M]^+$ (100), 232 $[M - 1]^+$ (34), 218 (33), 167 (88), 149 (71), 113 (36), 112 (40). Found, %: C 61.73; H 4.80; N 6.09. $C_{12}H_{11}NO_4$. Calculated, %: C 61.80; H 4.75; N 6.01.

The reaction with 2,3-dihydroxynaphthazarin (**XVa**) took 5 min. The product was extracted into ethyl acetate (3×10 ml), the extract was dried over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was separated by preparative thin-layer chromatography using hexane–acetone (2:1) as eluent, a fraction with R_f 0.72 being collected. Yield 65%. According to the ^{1}H NMR data, the product was a mixture of isomers **XX** and **XXI** at a ratio of 1:1.5 (their structures were assigned arbitrarily).

2-Amino-3,5,8-trihydroxy-6-methyl-1,4-dihydronaphthalene-1,4-dione (XX). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.41 d (3H, CH_3, J = 1.0 Hz), 5.35 br.s (2H, NH_2), 7.22 q (1H, 7-H, J = 1.0 Hz), 8.54 br.s (1H, OH), 11.64 s and 11.75 s (1H each, α-OH).

3-Amino-2,5,8-trihydroxy-6-methyl-1,4-dihydronaphthalene-1,4-dione (XXI). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.39 d (3H, CH_3, J = 1.0 Hz), 5.12 br.s (2H, NH_2). 7.31 q (1H, 7-H, J = 1.0 Hz), 8.54 br.s (1H, OH), 11.22 s and 12.08 s (1H each, α-OH).

The reaction with 2,3-dihydroxynaphthazarin **XVb** was complete in 5 min. After acidification, a finely crystalline material separated and was filtered off and washed with water (3×3 ml). The products were separated by column chromatography on Toyopearl HW-40 TSK gel using 40% ethanol containing 0.6% of formic acid as eluent. We thus isolated 2(3)-amino-3(2)-hydroxynaphthazarins **I** and **II**.

3-Amino-7-ethyl-2,5,6,8-tetrahydroxy-1,4-dihydronaphthalene-1,4-dione (I, echinamine A). Yield 48%, dark brown powder, mp 245–246°C (from acetone) [2]. IR spectrum, ν, cm^{-1}: 3522, 3445, 3379 (NH_2, β-OH); 1650, 1603 (C=O); 1589, 1562 (NH_2, C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.14 t (3H, CH_3, J = 7.5 Hz), 2.69 q (2H, CH_2, J = 7.5 Hz), 5.36 br.s (2H, NH_2), 8.49 br.s and 9.20 br.s (1H each, β-OH), 12.62 s and 13.03 s (1H each, α-OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.9 (CH_3), 16.3 (CH_2), 102.6 (C^{8a}), 108.6 (C^{4a}), 126.5 (C^7), 132.4 (C^3), 137.0 (C^2), 152.3 (C^6), 154.0 (C^5), 161.0 (C^8), 177.4 (C^4), 181.7 (C^1). Mass spectrum, m/z (I_{rel}, %): 266 $[M + 1]^+$ (44), 265 $[M]^+$ (100), 264 (15), 223 (12), 222 (40). Found: m/z 265.0598 $[M]^+$. $C_{12}H_{11}NO_6$. Calculated: M 265.0586.

2-Amino-7-ethyl-3,5,6,8-tetrahydroxy-1,4-dihydronaphthalene-1,4-dione (II, echinamine B). Yield 47%, dark brown needles, mp 265–267°C (from acetone), [2]. IR spectrum, ν, cm^{-1}: 3518, 3460, 3398 (NH_2, β-OH); 1664, 1603 (C=O); 1580, 1560 (NH_2, C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.13 t (3H, CH_3, J = 7.5 Hz), 2.67 q (2H, CH_2, J = 7.5 Hz), 5.81 br.s (2H, NH_2), 8.36 br.s and 9.44 br.s (1H each, β-OH), 13.02 s (1H each, α-OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.9 (CH_3), 16.6 (CH_2), 103.9 (C^{8a}), 107.6 (C^{4a}), 124.4 (C^7), 134.8 (C^2), 135.1 (C^3), 151.4 (C^6), 154.0 (C^5), 163.2 (C^8), 176.6 (C^1), 178.7 (C^4). Mass spectrum, m/z (I_{rel}, %): 266 $[M + 1]^+$ (44), 265 $[M]^+$ (100), 264 (15), 223 (12), 222 (40). Found: m/z 265.0598 $[M]^+$. $C_{12}H_{11}NO_6$. Calculated: M 265.0586.

4-Ethyl-6,9-dihydroxy-2,2-dimethylnaphtho-[1,2-*d*]oxazol-5(2*H*)-one (XVIIIa). A solution of 47 mg (0.2 mmol) of aminojuglone **XVIIb** in 10 ml of acetone containing a catalytic amount of sulfuric acid was kept for 72 h at room temperature. The solvent was removed under reduced pressure, and the residue was purified by TLC using hexane–acetone (2:1) as eluent. Yield 95%, yellow needles, mp 134°C. IR spectrum, ν, cm^{-1}: 3219 (α-OH), 2856 (CH_3), 1663 (C=O), 1600 (C=N), 1571 (C=C). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.14 t (3H, CH_3, J = 7.5 Hz), 1.74 s (6H, CH_3), 2.52 q (2H, CH_2, J = 7.5 Hz), 7.15 d (1H, 7-H, J = 9.3 Hz), 7.18 d (1H, 8-H, J = 9.3 Hz), 9.68 br.s (1H, α-OH), 12.76 s (1H, α-OH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.8 (CH_3), 16.2 (CH_2), 26.3 ($2CH_3$), 108.1 (C^{9a}), 112.4 (C^{5a}), 116.1 (C^4), 116.9 (C^2), 123.8 (C^7), 125.7 (C^8), 151.7 (C^9), 155.8 (C^{9b} or C^6), 156.0 (C^6 or C^{9b}), 160.3 (C^{3a}), 190.3 (C^5). Mass spectrum, m/z (I_{rel}, %): 273 $[M]^+$ (100), 274 $[M + 1]^+$ (18), 272 $[M - 1]^+$ (33), 259 (20), 258 (87), 149 (9). Found, %: C 65.87; H 5.60; N 5.14. $C_{15}H_{15}N_1O_4$. Calculated, %: C 65.91; H 5.54; N 5.13.

5-Ethyl-7,10-dihydroxy-1,2,3,4-tetrahydrobenzo-[*f*]quinoxalin-6(10b*H*)-one (XIXa). A solution of 50 mg (0.2 mmol) of hydroxynaphthazarin **XIVb**, 560 mg (4 mmol) of ethane-1,2-diamine hydrochloride, and 640 mg (11 mmol) of potassium hydroxide in 7 ml of water was stirred for 3 h at 65°C. The mixture was acidified to pH 3 with 5% hydrochloric acid, and the finaly crystalline precipitate was filtered off, washed with water (3×3 ml), and dried under reduced pressure over NaOH. The product was purified by TLC using benzene as eluent. Yield 85%, violet powder, mp 115°C. ^{1}H NMR spectrum (DMSO-d_6), δ,

ppm: 0.98 t (3H, CH_3, J = 7.3 Hz), 2.44 q (2H, CH_2, J = 7.3 Hz), 3.42 m (2H, C**H**$_2$NH), 3.85 t (2H, NCH_2, J = 6.2 Hz), 6.94 d (1H, 8-H, J = 9.7 Hz), 6.98 d (1H, 9-H, J = 9.7 Hz), 7.66 br.s (1H, NH), 13.40 br.s (1H, α-OH), 13.91 s (1H, α-OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 12.1 (CH_3), 15.2 (CH_2), 37.3 (C^3), 42.5 (C^2), 108.3 (C^{6a}), 109.2 (C^{10a}), 114.3 (C^5), 128.3 (C^9), 130.1 (C^8), 142.6 (C^{4a}), 150.3 (C^{10b}), 161.0 (C^{10}), 164.8 (C^7), 178.9 (C^6). Mass spectrum, m/z (I_{rel}, %): 258 $[M]^+$ (57), 257 $[M - 1]^+$ (33), 256 $[M - 2]^+$ (81), 227 (30), 213 (32), 194 (30), 167 (40), 157 (37), 141 (44), 129 (74), 127 (47), 115 (53), 113 (58). Found, %: C 65.08; H 5.50; N 10.87. $C_{14}H_{14}N_2O_3$. Calculated, %: C 65.11; H 5.46; N 10.85.

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