The chemistry of naphthazarin derivatives

3.* Synthesis of the dideoxy analog of islandoquinone

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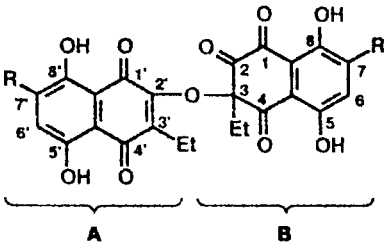
The 7,7′-dideoxy analog of islandoquinone, binaphthazarin of a new structural type, bearing a 2-oxo-2,3-dihydro-1,4-naphthoquinone moiety was synthesized. The carbonyl group at the C(2) atom of this binaphthazarin easily adds water to give the corresponding *gem*-diol. Comparison of the spectral characteristics of the prepared diol and islandoquinone made it possible to elucidate more precisely the structure of the latter.

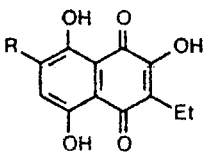
Key words: *Cetraria islandica* var. *polaris*, islandoquinone, 2-oxo-2,3-dihydro-1,4-naphthoquinone, 2,2-dihydroxy-2,3-dihydro-1,4-naphthoquinone, naphthazarin, *gem*-diol, oxidative coupling, tautomerism.

Recently, isolation of an islandoquinone from the red thallus tips of the lichen *Cetraria islandica* var. *polaris* has been reported; for this compound, structure **1** was proposed. Compound **1** is a binaphthazarin of a new structural class; the 1,4-naphthoquinone and 2,3-dihydro-1,4-naphthoquinone moieties in its molecule are linked by an ether bridge. Retrosynthetic analysis of the structure of islandoquinone (**1**) shows that this compound results from oxidative coupling of two molecules of 3-ethyl-2,7-dihydroxynaphthazarin (**2**). In order to justify practically this approach to the synthesis of biquinone **1**, we prepared its 7,7′-dideoxy-analog **3** using 3-ethyl-2-hydroxy-1,4-naphthazarin (**4**) as the key intermediate.



A **B**

1, 3

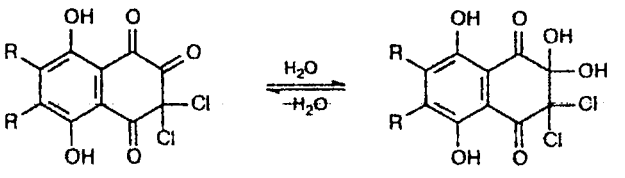


2, 4

R = OH (**1**, **2**), H (**3**, **4**)

Biquinone **3** was chosen as the object of the synthesis not only due to the fact that substrate **4** is relatively available but also in order to elucidate some characteristic features of the structure of islandoquinone itself. Thus the position of the ethyl substituent at the C(3′) atom in the naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) moiety (**A**) of biquinone **1** was chosen arbitrarily, because the spectral methods used in establishing the structure of islandoquinone did not allow the positions of C(3′) and C(6′) to be unambiguously distinguished.[2] At the same time, the presence of only one β-hydroxy group (at the C(2) atom) in the molecule of naphthazarin **4** predetermines the position of the ethyl radical at the C(3′) atom in moiety **A** of binaphthazarin **3**; therefore, comparison of the spectral characteristics of compounds **1** and **3** would confirm or correct the structure proposed for islandoquinone. The question of the tautomeric form in which the naphthazarin moiety **A** of biquinone **1** exists also remains open.

In a recent study,* we showed that 2-oxo-2,3-dihydronaphthazarins of type **5** readily add water at the carbonyl group at the C(2) atom to give *gem*-diols of the general formula **6**.



5 **6**

R = H, Cl, Me

* For Part 2, see Ref. 1.

* The study is being prepared for publication.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 947—952, May, 1999.

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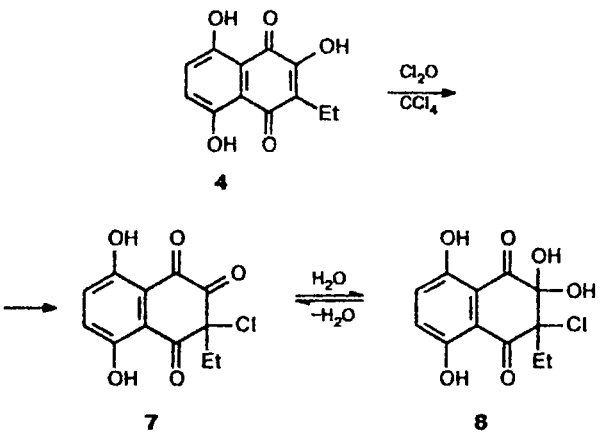
Scheme 1



The formal structural similarity of 2-oxo-2,3-dihydronaphthazarins of type **5** and moiety **B** of binaphthazarin **3** suggests that this compound would add water at the oxo group at the C(2) atom to give the corresponding *gem*-diol. In view of the probability of this hydration, we synthesized a number of model compounds which would ensure the fullest possible assignment of signals in the ^{1}H NMR spectra of the products. First, 3-chloro-3-ethyl-2-oxo-2,3-dihydro-1,4-naphthazarin (**7**) was prepared by the reaction of hydroxynaphthazarin **4** with Cl_2O (Scheme 1).

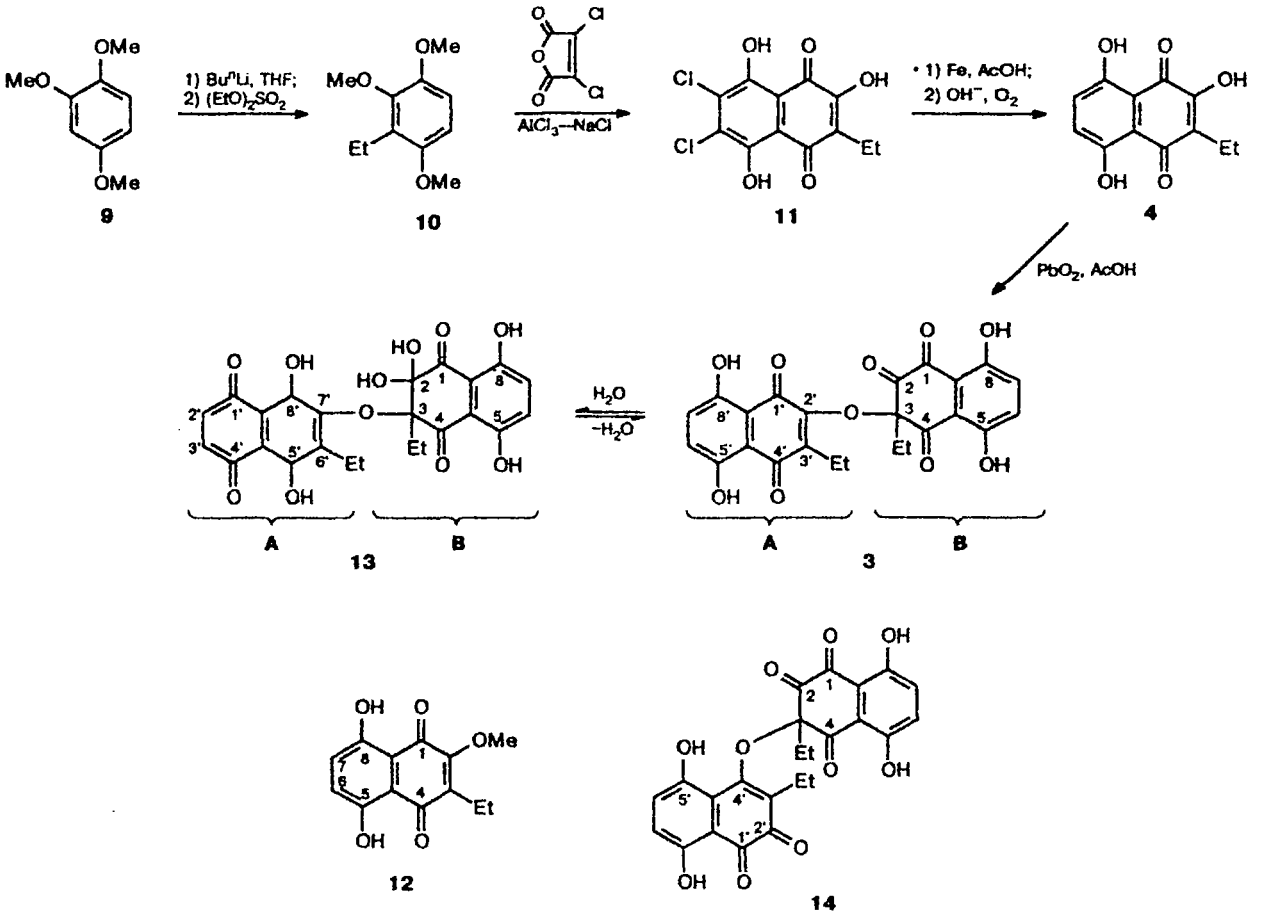
The IR spectrum of compound **7** recorded in anhydrous $CHCl_3$, in addition to the intense absorption band at 1657 cm^{-1}, due to the C=O groups in the dihydronaphthazarin fragment involved in an intramolecular hydrogen bond (IMHB), exhibits an intense band at 1748 cm^{-1}, which implies the presence of a C=O group not involved in IMHB. During storage of the solution of 2-oxo-1,4-naphthazarin **7** in moist chloroform, an equilibrium with the corresponding *gem*-diol **8** is established (see Scheme 1). In acetone containing a slight amount of water, this equilibrium (according to the ^{1}H NMR spectra) is completely shifted to diol **8**, which can be isolated and characterized upon removal of the solvent. The IR spectrum of diol **8**, recorded immediately after its dissolution in $CHCl_3$, does not contain the absorption band at 1748 cm^{-1}, typical of compound **7**, and the two *gem*-OH groups are responsible for one nonresolved broad band at 3500 cm^{-1}. The ^{1}H NMR spectrum of compound **8** contains signals at δ 4.23 and 4.60 due to the protons of the geminal hydroxy groups at the C(2) atom. The intensity of the molecular ion $[M]^+$ peak with *m/z* 286/288 in the mass spectrum of diol **8** is low, and its multiplicity points to the presence of one Cl atom in the molecule. Thorough dehydration of a mixture of compounds **7** and **8**, prepared from hydroxynaphthazarin **4**, over P_2O_5 *in vacuo* and with heating affords 2-oxo-derivative **7**.

As the initial substrate in the synthesis of the target compound **3** (Scheme 2), we chose 1,2,4-trimethoxybenzene (**9**). Lithiation of compound **9** on treatment with *n*-butyllithium in THF followed by treatment of the Li derivative with diethyl sulfate gave 3-ethyl-1,2,4-trimethoxybenzene (**10**). Cycloacylation of ether **10** with dichloromaleic anhydride in the $AlCl_3$—NaCl melt afforded dichloronaphthazarin **11**, which was converted into naphthazarin **4** by reductive dehalogenation (see Scheme 2).

Oxidative coupling of hydroxynaphthazarin **4** on treatment with PbO_2 in acetic acid[3] gave, after chromatographic separation, a product which, judging from the ^{1}H NMR spectrum (in $CDCl_3$), was a mixture of two binaphthazarins present in ~2.5 : 1.0 ratio. In particular, the proton signals displayed in the aromatic region of the spectrum can be divided, regarding their intensity, into two groups (Fig. 1). Comparison of the chemical shifts of the aromatic protons in the major component of the mixture (δ 7.08, 7.24 and δ 7.42, 7.47) (Table 1) with the chemical shifts of the corresponding protons in model compounds **12** (δ 7.20, 7.22) and **7** (δ 7.40, 7.47) led to the assumption that the major reaction product is binaphthazarin **3**. Analysis of the proton signals for the minor product and comparison of their chemical shifts with the corresponding chemical shifts in the ^{1}H NMR spectra of model compounds **8** and **12** showed that diol **13** is the minor product of the mixture.

When the product mixture obtained upon oxidative coupling of hydroxynaphthazarin **4** was thoroughly dehydrated over P_2O_5 *in vacuo* at an elevated temperature, binaphthazarin **3** was formed. The ^{1}H NMR spectrum of compound **3** recorded in anhydrous $CDCl_3$ completely coincides with the spectrum of the major component of the mixture. In addition to the features discussed above, the ^{1}H NMR spectrum of compound **3** (see Table 1) contains the signals at δ 11.48, 11.45, 13.02, and 12.03 for the protons of the four *peri*-hydroxy groups (at positions 5, 8, 5′, and 8′, respectively), which rules out the alternative *ortho*-quinone structure **14**, similar to "lapachol peroxide".[4] In the case of structure **14**, the signal of the proton of the hydroxy group at C(5′) would occur at about δ ~9.5.[5] In addition to the absorption band of the C=O group of moiety **A** (1594 cm^{-1}), the IR spectrum of compound **3** recorded in anhydrous $CDCl_3$ contains bands at 1642 cm^{-1} and 1664 cm^{-1}, which are due to the carbonyl groups of moiety **B** involved in IMHB, and a band at 1751 cm^{-1}, pointing to the presence of a C=O group not involved in an IMHB. The presence of an intense band at 1263 cm^{-1} and a medium-intensity band at 1040 cm^{-1} confirms the ether nature of the linkage between moieties **A** and **B**. The mass spectrum of compound **3** exhibits a low-intensity signal with *m/z* 466 (3%) $[M]^+$; the peak of an ion with *m/z* 234 (100%), corresponding to the molecular ion of compound **4**, is the most intense in the spectrum.

Scheme 2



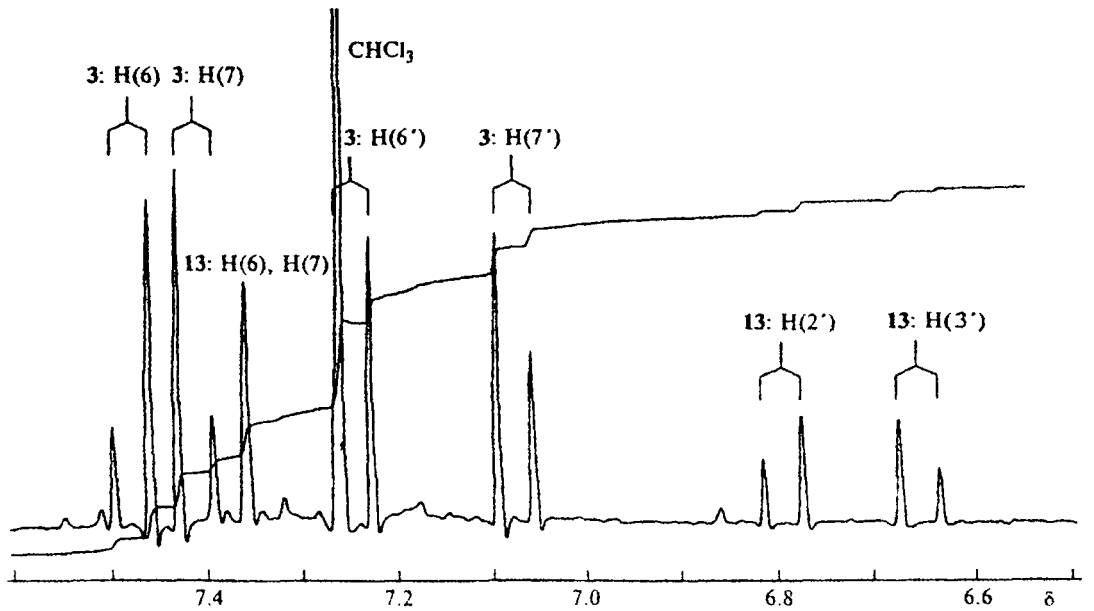


Fig. 1. ^1H NMR spectrum of a mixture of products 3 and 13 in $CDCl_3$ (the region of aromatic protons).

Table 1. ^{1}H NMR spectra of compounds **3**, **7**, **8**, **12**, and **13** (in $CDCl_3$)

Compound, moiety	δ (*J*/Hz)						
	C(2)—OH	C(5)—OH, C(5′)—OH	H(6), H(6′) [H(2′)]	H(7), H(7′) [H(3′)]	C(8)—OH, C(8′)—OH	CH_2	CH_3
3, A	—	13.02 (s, 1 H)	7.24 (d, 1 H, *J* = 9.7)	7.08 (d, 1 H, *J* = 9.7)	12.03 (s, 1 H)	2.83 (q, 2 H, *J* = 7.5)	1.28 (t, 3 H, *J* = 7.5)
3, B	—	11.48 (s, 1 H)	7.47 (d, 1 H, *J* = 9.7)	7.42 (d, 1 H, *J* = 9.7)	11.45 (s, 1 H)	2.16 (m, 2 H)	1.08 (t, 3 H, *J* = 7.5)
13, A	—	13.01 (s, 1 H)	[6.78] (d, 1 H, *J* = 10.5)	[6.66] (d, 1 H, *J* = 10.5)	—	2.93 (m, 2 H)	1.35 (t, 3 H, *J* = 7.5)
13, B	5.44 (br.s, 2 H)	11.11 (s, 1 H)	7.36 (s, 2 H, H(6), H(7))		10.88 (s, 1 H)	1.78, 2.33 (both dq, each 1 H, ^1J = 15.0, ^2J = 7.5)	1.03 (t, 3 H, *J* = 7.5)
12	—	12.77 (s, 1 H)	7.22 (d, 1 H, *J* = 9.4)	7.20 (d, 1 H, *J* = 9.4)	12.33 (s, 1 H)	2.62 (q, 2 H, *J* = 7.6)	1.13 (t, 3 H, *J* = 7.6)
7	—	11.84 (s, 1 H)	7.47 (d, 1 H, *J* = 10.0)	7.40 (d, 1 H, *J* = 10.0)	11.70 (s, 1 H)	2.45 (m, 2 H)	1.07 (t, 3 H, *J* = 7.6)
8	4.23 (br.s, 1 H); 4.60 (br.s, 1 H)	11.45 (s, 1 H)	7.36 (d, 1 H, *J* = 9.6)	7.32 (d, 1 H, *J* = 9.6)	10.79 (s, 1 H)	2.28 (m, 2 H)	1.08 (t, 3 H, *J* = 7.6)

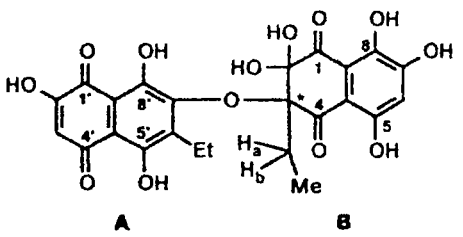
Having been dissolved in moist chloroform, compound **3** soon adds water at the oxo group at position 2 to give *gem*-diol **13**; however, this process is reversible, and, according to the ^{1}H NMR spectrum, the equilibrium mixture corresponds to **3** : **13** ≈ 2.5 : 1.0 (see Scheme 2). The ^{1}H NMR spectrum of the resulting mixture exhibits a broad signal at δ 5.44, due to the two protons of the geminal hydroxy groups at C(2), while the chemical shifts of protons in moiety **B** of the compound having presumably structure **13** (δ 7.36, 2 H) are in good agreement with the chemical shifts of the signals of aromatic protons in diol **8** (δ 7.32, 7.36). However, the comparison of the chemical shifts of the protons at C(6) and C(7) in model compound **12** (δ 7.20, 7.22) and at C(6′) and C(7′) in binaphthazarin **3** (δ 7.08, 7.24) with the chemical shifts of the protons in the naphthazarin moiety **A** of product **13** (δ 6.66, 6.78) led to the conclusion that the latter have the quinoid nature and, therefore, moieties **A** in compounds **3** and **13** occur in different tautomeric forms (see Scheme 2). In acetone, this keto—*gem*-diol equilibrium is shifted almost entirely to diol **13**. The ^{1}H NMR spectrum in acetone-d_6 fully confirms the conclusions concerning the structure of compound **13** drawn from the analysis of its mixture with binaphthazarin **3** in $CDCl_3$ (see above). In particular, the ^{1}H NMR spectrum in acetone-d_6, unlike that in $CDCl_3$, exhibits signals for all four α-hydroxy groups in compound **13** (see Table 1 and Experimental).

The compositions of products **3**, **7**, **8**, and **13** were confirmed by the data of elemental analysis.

When comparing the structures of islandoquinone and biquinones **3** and **13**, the signals of the ethyl group protons were chosen as the reference ^{1}H NMR signals. We proceeded from the fact that the presence (or absence) of hydroxy groups at positions 7 and 7′ has a less pronounced effect on the chemical shifts of the protons in the ethyl groups at positions 3 and 3′ than on the chemical shifts of other protons in these compounds. Meanwhile, the presence of carbonyl or *gem*-diol groups at position 2 in compounds **1**, **3**, and **13** should have a substantial effect on the signals of the ethyl group protons. The signals of these protons in the ^{1}H NMR spectrum of 2-oxo-2,3-dihydro-derivative **3**, recorded in $CDCl_3$, occur at δ 1.28 (CH_3), 2.83 (CH_2) (moiety **A**) and δ 1.08 (CH_3), 2.16 (CH_2) (moiety **B**), and those for diol **13** are at δ 1.35 (CH_3), 2.93 (CH_2) (moiety **A**) and δ 1.03 (CH_3), 1.78 (CH_a), 2.33 (CH_b) (moiety **B**, see Table 1). The corresponding signals of islandoquinone (in $CDCl_3$) occur at δ 1.37 (CH_3), 2.96 (CH_2) and δ 1.05 (CH_3), 1.79 (CH_a), 2.36 (CH_b),* which virtually coincide with the corresponding signals of diol **13**; this implies that in a chloroform solution, this compound exists as structure **15**. This assumption is confirmed by the fact that the ^{1}H NMR spectrum of islandoquinone exhibits a diffuse signal at δ 5.36, corresponding to the protons of the two geminal hydroxy groups at the C(2) atom. The formation of diol **15** from compound **1**, as in other similar cases, becomes possible due to the presence of water in the initial sample or the solvent. Therefore, it can be assumed that owing to the normal

* The ^{1}H NMR spectrum of islandoquinone in $CDCl_3$ was kindly provided by an author of Ref. 2.

presence of water in natural objects, structure **15** is the most probable form of existence of islandoquinone.



15

It should be noted that the naphthazarin moiety (A) in the hypothetical structure **15** occurs in a different tautomeric form than that in compound **1**. This directly follows from a comparison of the ^{1}H NMR spectra of islandoquinone and diol **13**. In addition, this conclusion is in full agreement with the empirical rule formulated by Moore and Scheuer for substituted naphthazarins.[6] Finally, comparison of the ^{1}H NMR spectra of the above-mentioned compounds made it possible to determine unambiguously the position of the ethyl substituent (at C(6′), structure **15**) in moiety A of islandoquinone. Apparently, the formation of compound **1** can be regarded as an artifact, occurring during isolation of the substance and its preparation for the analysis, most of all, during the operations performed at elevated temperatures (evaporation, crystallization, drying).[2] However, the structure of islandoquinone cannot be considered to be ultimately proven; additional study of the natural product itself with allowance for the known properties of its 7,7′-dideoxy analog are needed.

Experimental

Melting points were determined on a Boetius hot stage and not corrected. IR spectra were recorded on a Specord M-82 spectrophotometer in $CHCl_3$ ($CDCl_3$). ^{1}H NMR spectra were measured on a Bruker WM-250 spectrometer (250 MHz) in $CDCl_3$ and acetone-d_6 using tetramethylsilane as the internal standard. MS (EI) were run on an LKB-9000S instrument with direct sample inlet and an ionizing energy of 70 eV. The course of the reaction was monitored and the purity of the obtained compounds was checked by TLC on Silufol UV-254 plates. The R_f values were determined by subjecting all the compounds obtained to chromatography in the hexane—acetone system (3 : 1). Individual compounds were isolated from product mixtures using a column with L 40/100 μm silica gel and the hexane—acetone gradient system (10 : 1 → 5 : 1) or using preparative TLC on plates (20×20 cm) with a nonfixed silica gel layer (5—40 μm) in the hexane—acetone system (3 : 1 or 4 : 1). The yields of the prepared compounds were not optimized.

3-Ethyl-1,2,4-trimethoxybenzene (10). A 1.6 *M* solution of Bu^{n}Li (45 mL, 72 mmol) in hexane was added dropwise with stirring in an argon atmosphere over a period of 50 min to a solution of commercial 1,2,4-trimethoxybenzene (**9**) (8.0 g, 48 mmol) in 35 mL of THF cooled to −30 °C. After the whole solution of Bu^{n}Li had been added, stirring was continued for 1.5 h; during this period, the mixture warmed up to −20 °C. The reaction mixture was cooled on an ice bath, $(EtO)_2SO_2$ (4.7 mL, 5.5 g, 36 mmol) was added dropwise, and the mixture was stirred for an additional 2 h at −20 °C and allowed to stand for ~18 h. Then the reaction mixture was poured into an ice—water mixture (250 mL) and extracted with ether. The extract was washed with water and brine, dried with $CaCl_2$, and concentrated to give an oil (8.9 g), containing, according to ^{1}H NMR data, 85% of the target product **10**. ^{1}H NMR ($CDCl_3$), δ: 1.12 (t, 3 H, CH_3, J = 7.5 Hz); 2.67 (q, 2 H, CH_2, J = 7.5 Hz); 3.78 (s, 3 H, OCH_3); 3.82 (s, 3 H, OCH_3); 3.83 (s, 3 H, OCH_3); 6.55 (d, 1 H, H arom., J = 8.7 Hz); 6.70 (d, 1 H, H arom., J = 8.7 Hz). Crude product **10** was used in the next synthesis step without purification.

6,7-Dichloro-3-ethyl-2,5,8-trihydroxy-1,4-naphthoquinone (11). At 140 °C, a mixture of 3-ethyl-1,2,4-trimethoxybenzene (**10**) (0.78 g, 4 mmol) and dichloromaleic anhydride (1.34 g, 8 mmol) was added with vigorous stirring to a melt consisting of anhydrous $AlCl_3$ (16.0 g, 120 mmol) and NaCl (3.2 g, 55 mmol), the temperature of the mixture was increased to 195 °C, and the melt was stirred for an additional 4 min. The reaction mixture was cooled, hydrolyzed with 5% HCl (200 mL), and allowed to stand for 12 h. The resulting crude product **11** was separated, washed with 50 mL of hot H_2O, dried, and purified on a column with silica gel. Yield 0.61 g (51%), m.p. 156—158 °C. ^{1}H NMR ($CDCl_3$), δ: 1.18 (t, 3 H, CH_3, J = 7.7 Hz); 2.66 (q, 2 H, CH_2, J = 7.7 Hz); 9.77 (br.s, 1 H, C(2)—OH); 12.07 (s, 1 H, C(8)—OH); 13.60 (s, 1 H, C(5)—OH). MS, m/z (I_{rel} (%)): 302/304/306 $[M]^+$ (71), 286/288/290 (83), 285/287/289 (65), 267/269 (45), 252/254 (35), 244/246 (31), 230 (100). Found (%): C, 47.64; H, 2.71. $C_{12}H_8Cl_2O_5$. Calculated (%): C, 47.55; H, 2.66.

3-Ethyl-2,5,8-trihydroxy-1,4-naphthoquinone (4). A mixture of dichloronaphthazarin **11** (303 mg, 1 mmol) and iron powder (560 mg, 10 mmol) in 30 mL of glacial AcOH was refluxed for 10 min. After cooling, the reaction mixture was filtered and the solvent was removed at a reduced pressure. The residue was treated with 5% NaOH up to pH 8—9, and the resulting mixture was stirred in air until the solution acquired a dark-blue color (15—40 min, TLC monitoring for acidified samples in the hexane—acetone (2 : 1) system). When the reaction had been completed, the mixture was acidified with 10% HCl to pH 4—5. The resulting precipitate of crude product **4** was separated by filtration or extracted with ether and subjected to column chromatography to give compound **4**. Yield 157 mg (67%), m.p. 188—190 °C (Ref. 7: m.p. 190.5—191.5 °C). ^{1}H NMR ($CDCl_3$), δ: 1.16 (t, 3 H, CH_3, J = 7.8 Hz); 2.62 (q, 2 H, CH_2, J = 7.8 Hz); 7.17 (d, 1 H, H arom., J = 9.8 Hz); 7.29 (d, 1 H, H arom., J = 9.8 Hz); 7.34 (br.s, 1 H, C(2)—OH); 11.50 (s, 1 H, C(8)—OH); 12.89 (s, 1 H, C(5)—OH). MS, m/z (I_{rel} (%)): 234 $[M]^+$ (100), 220 (8), 219 (11), 191 (33), 188 (10). Found (%): C, 61.38; H, 4.39. $C_{12}H_{10}O_5$. Calculated (%): C, 61.54; H, 4.30.

3-Ethyl-5,8-dihydroxy-2-methoxy-1,4-naphthoquinone (12) Compound **12** was prepared by treatment of a solution of compound **4** in ether with a solution of diazomethane in ether.[8] The data of the ^{1}H NMR spectrum are given in Table 1.

3-Chloro-3-ethyl-5,8-dihydroxy-2-oxo-2,3-dihydro-1,4-naphthoquinone (7). A dilute solution of Cl_2O in CCl_4 was slowly added dropwise, at 20 min intervals, to a stirred solution of naphthazarin **4** (47 mg, 0.2 mmol) in 10 mL of CCl_4.[9] The course of the reaction was monitored by TLC in the hexane—acetone (4 : 1) system. After the reaction, the mixture was concentrated and the crude product was subjected to preparative TLC in the hexane—acetone (3 : 1) system; the

zone with R_f 0.34 was isolated. The product thus obtained was kept *in vacuo* over P_2O_5 for 3 h at 110 °C to give compound **7**, yield 44 mg (82%), m.p. 90—92 °C. IR, ν/cm^{-1}: 3200 (α-O—H); 1748, 1657 (C=O); 1589 (C=C). The data of the ^1H NMR spectrum are given in Table 1. Found (%): C, 53.45; H, 3.46. $C_{12}H_9ClO_5$. Calculated (%): C, 53.65; H, 3.38.

3-Chloro-3-ethyl-2,2,5,8-tetrahydroxy-2,3-dihydro-1,4-naphthoquinone (8). 2-Oxo-2,3-dihydronaphthazarin **7** (27 mg, 0.1 mmol) was dissolved in 5 mL of acetone containing 1% H_2O. After 1 h, the solvent was removed *in vacuo* at ~20 °C to give product **8**, m.p. 86—87 °C (with decomp.). IR, ν/cm^{-1}: 3500 (*gem*-O—H); 3200 (α-O—H); 1663 (C=O); 1594 (C=C). The data of the ^1H NMR spectrum are given in Table 1. MS, m/z (I_{rel} (%)): 286/288 $[M]^+$ (5), 269/271 (13), 268/270 (80), 240/242 (45), 235 (15), 234 (100). Found (%): C, 50.06; H. 3.93. $C_{12}H_{11}ClO_6$. Calculated (%): C, 50.28; H, 3.87.

3-Ethyl-5,8-dihydroxy-3-*O*-(3-ethyl-5,8-dihydroxy-1,4-naphthoquinon-2-yloxy)-2-oxo-2,3-dihydro-1,4-naphthoquinone (3). Freshly prepared PbO_2 [16] (143 mg, 0.6 mmol) was added with vigorous shaking to a solution of hydroxynaphthazarin **4** (70 mg, 0.3 mmol) in 2 mL of glacial AcOH heated to boiling. The reaction mixture was vigorously shaken for 3—5 min, cooled, and filtered. The filtrate was concentrated at a temperature below 70 °C; the residue was diluted with water (30 mL) and extracted with AcOEt (3×10 mL). The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. Preparative TLC of the residue in the hexane—acetone (4 : 1) system resulted in separation of two zones. The first zone with R_f 0.50 contained recovered naphthazarin **4**, yield 31 mg (44%). The second zone with R_f 0.40 was dried *in vacuo* over P_2O_5 for 5 h at ~80 °C to give product **3**, yield 24 mg (62% based on reacted **4**), m.p. 94—96 °C. IR, ν/cm^{-1}: 2980, 2700 (O—H); 1751, 1664, 1642, 1594 (C=O); 1567 (C=C); 1456, 1288, 1263, 1192, 1156, 1040. The data of the ^1H NMR spectrum are given in Table 1. MS, m/z (I_{rel} (%)): 466 $[M]^+$ (3), 465 $[M - 1]^+$ (4), 235 (22), 234 (100), 219 (14), 205 (10), 191 (63), 189 (11), 188 (22). Found (%): C, 61.68; H, 3.99. $C_{24}H_{18}O_{10}$. Calculated (%): C, 61.80; H, 3.89.

3-Ethyl-2,2,5,8-tetrahydroxy-3-*O*-(6-ethyl-5,8-dihydroxy-1,4-naphthoquinon-7-yloxy)-2,3-dihydro-1,4-naphthoquinone (13). Binaphthazarin **3** (23 mg, 0.05 mmol) was dissolved in 5 mL of acetone containing 1% H_2O. After 1 h, the solvent was removed *in vacuo* at ~20 °C to give product **13**, m.p. 90—92 °C (with decomp.). The data of the ^1H NMR spectrum in $CDCl_3$ are given in Table 1. ^1H NMR (acetone-d_6), δ: 1.04 (t, 3 H, CH_3, J = 7.5 Hz); 1.34 (t, 3 H, CH_3, J = 7.5 Hz); 2.03 (dq, 1 H, CH_a, ^1J = 15.0 Hz, ^2J = 7.5 Hz); 2.36 (dq, 1 H, CH_b, ^1J = 15.0 Hz, ^2J = 7.5 Hz); 2.92 (m, 2 H, CH_2); 3.32 (br.s, 1 H, OH); 3.78 (br.s, 1 H, OH); 6.71 (d, 1 H, quinone H, J = 10.5 Hz); 6.89 (d, 1 H, quinone H, J = 10.5 Hz); 7.48 (s, 2 H, H(6), H(7) arom.); 7.98 (br.s, 1 H, OH); 11.04 (s, 1 H, OH); 11.11 (s, 1 H, OH); 13.11 (s, 1 H, OH). Found (%): C, 59.81; H, 4.08. $C_{24}H_{20}O_{11}$. Calculated (%): C, 59.50; H, 4.16.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-15-97316).

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Received September 21, 1998;
in revised form November 24, 1998