Synthesis and structure elucidation of oxidative coupling products of 2-hydroxy-1,4-naphthoquinones

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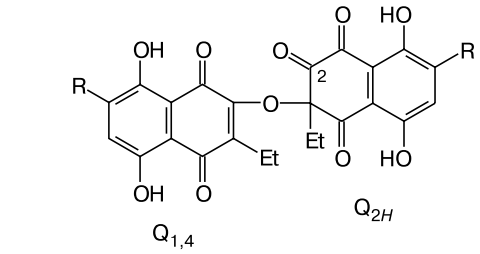
2,3-Dihydro-3-*O*-(1,4-naphthoquinon-2-yl)-2-oxo-1,4-naphthoquinones are the products of oxidative coupling of substituted 2-hydroxy-1,4-naphthoquinones (regardless of the presence of *peri*-hydroxy groups in their structures) under the action of lead dioxide.

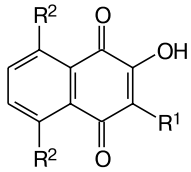
Key words: 2-hydroxy-1,4-naphthoquinone, 2,5(8)-dihydroxy-1,4-naphthoquinone, 2,5,8-trihydroxy-1,4-naphthoquinone, lead dioxide, oxidative coupling, 2,3-dihydro-3-*O*-(1,4-naphthoquinon-2-yl)-2-oxo-1,4-naphthoquinone, density functional theory.

The isolation of islandoquinone (**1a**) from *Cetraria islandica* lichen has been reported rather recently.[1] Compound **1a** is binaphthazarin of the new structural type in which the 2,3-dihydro-1,4-naphthoquinonoid (Q_{2H}) and 1,4-naphthoquinonoid ($Q_{1,4}$) fragments are linked through the ether bond. The structure of biquinone **1a** was determined from the data of UV and IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry. To refine some structural features of islandoquinone, its didesoxy analog **1b** was synthesized.[2] The key step in the synthesis of binaphthazarin **1b** is the oxidative coupling of hydroxynaphthazarin **2a** under the action of PbO_2 in acetic acid. This reaction has been used previously[3] in the synthesis of binaphthoquinones **3a,b** in which the Q_{2H} fragment is linked with the 1,2-naphthoquinonyl substituent ($Q_{1,2}$) through the ether bond.[4] In this case, lapachol (**2b**) and lawsone derivative **2c**, respectively, were the initial hydroxynaphthoquinones. Chemical methods were used to determine the structure of the Q_{2H} fragment of biquinones **3a**,**b**. The choice between the $Q_{1,4}$ fragment and alternative $Q_{1,2}$ was made (in favor of the latter) on the basis of the UV spectral data.[4]

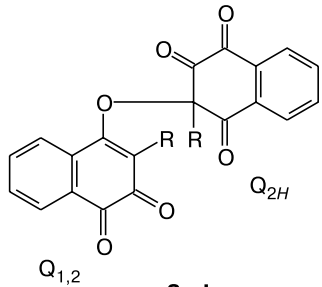


$Q_{1,4}$ Q_{2H}

1a,b



2a—c



$Q_{1,2}$ Q_{2H}

3a,b

1: R = OH (**a**), H (**b**)
2: R^1 = Et, R^2 = OH (**a**); R^1 = $CH_2CH{=}CMe_2$, R^2 = H (**b**); R^1 = *n*-C_5H_{11}, R^2 = H (**c**)
3: R = $CH_2CH{=}CMe_2$ (**a**), *n*-C_5H_{11} (**b**)

Since the general structure of the $Q_{1,2}$—Q_{2H} type was ascribed to binaphthoquinones **3a,b** and that of the $Q_{1,4}$—Q_{2H} type was ascribed to binaphthazarins **1a,b**, a question arises about the influence of structural features of the starting 2-hydroxy-1,4-naphthoquinones on the structures of their oxidative coupling products.

To answer this question, we synthesized and studied the structures of the oxidative coupling products of 2-hydroxy-1,4-naphthoquinones with and without the hydroxy group in the *peri*-position. The radical alkylation of 2-hydroxy- (**4a**), 2,5-dihydroxy- (**4b**), and 2,8-dihydroxy-1,4-naphthoquinones (**4c**) under the action of propionyl peroxide under the conditions of its thermal decomposition afforded ethyllawsone **2d** and the corresponding hydroxyethyljuglones **2e,f** (Scheme 1).

Compounds **2d—f** underwent oxidative coupling under the action of lead dioxide in acetic acid. The structures of the synthesized products were studied by UV and IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and quantum chemical methods.*

* Instability of the binaphthoquinones under study in the solid state impedes analyses of their structures by the X-ray diffraction method.

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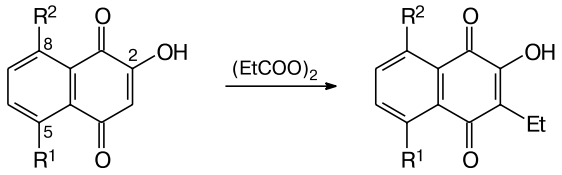
Scheme 1



4a—c **2d—f**

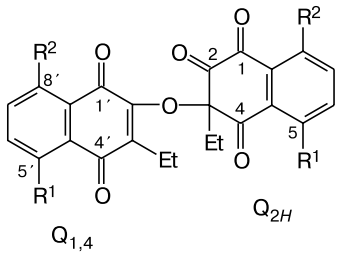
$R^1 = R^2 = H$ (**4a, 2d**); $R^1 = OH$, $R^2 = H$ (**4b**, **2e**); $R^1 = H$, $R^2 = OH$ (**4c**, **2f**)

The mass spectra and ^1H NMR spectra indicate that the structures of the oxidative coupling products of 2-hydroxy-1,4-naphthoquinones **2d—f** are dimeric. The IR spectra of these compounds contain absorption bands of the carbonyl groups of the quinonoid and conjugated with the aromatic ring dihydroquinonoid fragments (see Experimental), absorption bands of the free C=O groups at 1752—1748 cm^{-1}, and the bands at 1287—1231 cm^{-1}, the latest indicate that the structures of the compounds under study contain the ether bond.[5] These data along with literature analogies[1,2,6,7] suggest that the structures of the products contain the 2,3-dihydro-2-oxo-1,4-naphthoquinonoid fragment. Thus, the compounds synthesized by the oxidative coupling of substrates **2d—f** are biquinones in which the naphthoid and 2,3-dihydro-1,4-naphthoquinonoid fragments are linked through the ether bond.

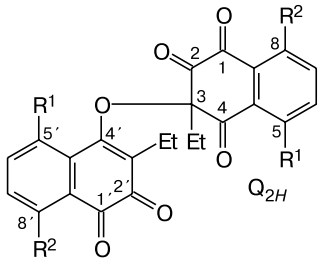
The presence of the signal from the proton of the *peri*-hydroxy group at the C(5′) atom of the quinonoid fragment (δ 12.26) in the ^1H NMR spectrum of the biquinone synthesized from hydroxyethyljuglone **2e** indicates that this fragment has the $Q_{1,4}$ structure and the whole compound has a structure of **1d**. In the case of alternative product **3d**, the signal from the proton of the *peri*-hydroxy group at the C(5′) atom in the $Q_{1,2}$ fragment would be observed at δ ~9.5.[8]

In the ^1H NMR spectrum of the product prepared from hydroxyethyljuglone **2f**, the chemical shift (CS) of the signal from the proton of the *peri*-hydroxy group of the quinonoid fragment at the C(8) atom is observed at δ 11.89 and is not characteristic.[2,8] The complete analysis of long-range correlations in 2D HMBC experiments made it possible to assign signals in the ^{13}C NMR spectra and make a choice between two alternative structures **3e** and **1e** in favor of the latter.

To determine the preferential direction of dimerization, we performed the quantum chemical* conformational analysis of compounds **1c—e** and **3c—e** due to which the relative energies $\Delta E_{\mathbf{1x,3x}}$ were estimated ($\Delta E_{\mathbf{1x,3x}} = E_{\mathbf{3x}} - E_{\mathbf{1x}}$; **x** = **c—e**). According to the DFT-PBE/3z



1c—e



3c—e

$R^1 = R^2 = H$ (**c**); $R^1 = OH$, $R^2 = H$ (**d**); $R^1 = H$, $R^2 = OH$ (**e**)

calculations, $\Delta E_{\mathbf{1c,3c}} \approx 17.57$ kcal mol^{-1}, $\Delta E_{\mathbf{1d,3d}} \approx 28.84$ kcal mol^{-1}, and $\Delta E_{\mathbf{1e,3e}} \approx 15.02$ kcal mol^{-1}.* Such a high difference in total energies assumes the predominant formation of products **1c—e** in the reaction (according to the calculations, the content of products **3c—e** in the reaction mixture is 10^{-12}—10^{-22}%).

The quantum chemical PBE/3z-GIAO//B3LYP/6-31 calculations of the NMR shielding constants showed that the difference in the CS of signals from the protons of the *peri*-hydroxy groups at the C(5′) atom of the quinonoid fragment and at the C(5) atom of the dihydroquinonoid fragment in compound **1d** is 0.65 ppm, which agrees well with the experimental value of the relative CS in the ^1H NMR spectrum (Δδ 0.75).

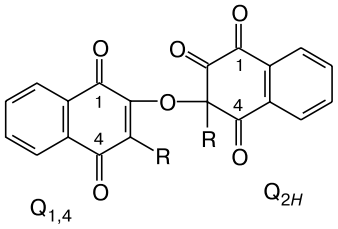
The total energy, which was calculated by us for the earlier determined structure of biquinone **1b**, is by ~27.39 kcal mol^{-1} lower than the total energy of the corresponding structure of the $Q_{1,2}$—Q_{2H} type. This indicates that the formation of a product of the $Q_{1,4}$—Q_{2H} type is a general rule for oxidative coupling reactions of compounds of this type.

Taking into account the structural similarity of naphthoquinone **2d**, lapachol (**2b**), and lawsone derivative **2c**, one can propose the structures for their oxidative coupling products. According to the quantum chemical calculations, the differences between the total energies of molecules **3a**,**b** and the corresponding structures of the $Q_{1,4}$—Q_{2H} type are 17.77 and 17.73 kcal mol^{-1}, respec-

* The detailed discussion of this problem is beyond the topic of the present work and will be given elsewhere. For description of the quantum chemical calculations, see Experimental.

* The additional theoretical analysis showed that the total Gibbs energies (ΔG_0) for the indicated structures only insignificantly (by 1—6%) differ from the calculated relative energies (ΔE_0).

tively. The ΔE values indicate that the structures of biquinones **3a,b** proposed earlier[4] are improbable and should be revised in favor of 2,3-dihydro-3-[(3-methylbut-2-enyl)-1,4-naphthoquinon-2-yloxy]-3-(3-methylbut-2-enyl)-2-oxo-1,4-naphthoquinone (**1f**) and 2,3-dihydro-3-(3-pentyl-1,4-naphthoquinon-2-yloxy)-2-oxo-3-pentyl-1,4-naphthoquinone (**1g**).



1f,g

R = $CH_2CH{=}CMe_2$ (**f**), *n*-C_5H_{11} (**g**)

Biquinones **1c—g** are probably the recombination products of radicals of the **A** and **B** types formed upon hydrogen atom abstraction from the starting substrates **2b—f** (Scheme 2).

Thus, the products of oxidative coupling of 3-ethyl-2-hydroxy- (**2d**), 3-ethyl-2,5-dihydroxy- (**2e**), and 3-ethyl-2,8-dihydroxy-1,4-naphthoquinones (**2f**) under the action of PbO_2 in acetic acid, as well as those of described hydroxynaphthazarin **2a** [2] and hydroxy-1,4-naphthoquinones **2b,c**,[4] are the corresponding biquinones **1b—g** containing the 1,4-naphthoquinonoid fragment.

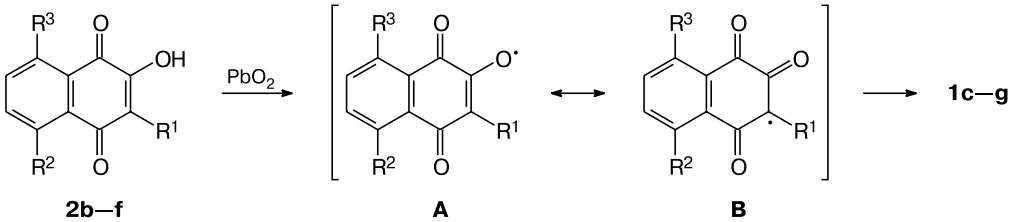
Experimental

Melting points of the synthesized compounds were determined on a Boetius apparatus and are uncorrected. IR spectra were recorded on a Bruker Vector 22 FTIR spectrometer in $CDCl_3$ and CCl_4. UV spectra were measured in a Cecil CE 7200 spectrophotometer in hexane in quartz cells with a layer thickness of 1.0 mm. NMR spectra were detected on Bruker Avance DPX-300 (300.13 (^{1}H) and 75 MHz (^{13}C)) and Bruker Avance DRX-500 (500.13 (^{1}H) and 125 MHz (^{13}C)) spectrometers in acetone-d_6 and $CDCl_3$ using Me_4Si as internal standard. The 2D COSY-45, HSQC, and HMBC experiments were carried out according to standard procedures at room temperature. The HMBC experiments were conducted with optimization for the long-range spin-spin coupling constant (SSCC) values equal to 2.5 and 10.0 Hz. Mass spectra (EI) were obtained on an LKB-9000S instrument with direct injection of a sample at an energy of ionizing electrons of 70 eV. The reaction course and purity of the synthesized compounds were monitored by TLC on Merck 60F-254 plates. The R_f values were determined in a hexane—acetone (3 : 1) system. Individual compounds were isolated from mixtures of the reaction products using preparative thin-layer chromatography (PTLC) on plates (20×20 cm) with the nonfixed 5—40-μm silica gel (H^+ form)[9] layer. The yields of the prepared compounds were not optimized. The starting 2-hydroxy-1,4-naphthoquinone (**4a**),[10] 2,5-dihydroxy-1,4-naphthoquinone (**4b**),[11] and 2,8-dihydroxy-1,4-naphthoquinone (**4c**)[11] were synthesized according to known procedures. The geometries of compounds **1b—g** and **3a—e** were optimized by the density functional theory (DFT) with the PBE correlation functional[12] in the triply-split valence basis set of atomic orbitals (3z) using the PRIRODA program[13] (DFT-PBE/3z). To estimate relative energies (ΔE), isomers characterized by the lowest total energy were selected of all possible conformations of compounds **1b—g** and **3a—e** differing in mutual orientation of the Q_{2H} and $Q_{1,2}$, $Q_{1,4}$ fragments and arrangement of the alkyl substituents relatively to these fragments. The relative energy for each compound was calculated with account for corrections to zero-point vibrational energies (ZPE) ($\Delta E = E_{tot}(Q_{1,2}{-}Q_{2H}) - E_{tot}(Q_{1,4}{-}Q_{2H})$, where $E_{tot} = E_0 + ZPE$ are the total energies, and E_0 are the total electronic energies). Relative CS were calculated using the PRIRODA program by the DFT method with the PBE functional in the triply-split valence basis set of Gauge-invariant atomic orbitals (GIAO) in geometries optimized by the GAMESS program package[14] using the DFT method with the B3LYP exchange-correlation functional[15] in the 6-31G basis set (PBE/3z-GIAO//B3LYP/6-31 calculations).

***C*-Alkylation of hydroxynaphthoquinones 4a—c with propionyl peroxide (general procedure).** Propionyl peroxide was added dropwise to a boiling solution of substrate **4a—c** (1.0 mmol) in Bu^tOH (30 mL), monitoring the reaction course by TLC. The reaction was stopped when the conversion reached ~80%. The solvent was removed *in vacuo*, and the residue was chromatographed by PTLC in a hexane—acetone (3 : 1) system.

3-Ethyl-2-hydroxy-1,4-naphthoquinone (2d) was synthesized by the ethylation of lawsone (**4a**). The yield was 155 mg (77%), R_f 0.43, m.p. 134—137 °C (*cf.* Ref. 16: m.p. 137.5—138.5 °C). IR (CCl_4), ν/cm^{-1}: 3406 m (β-OH); 1661 vs, 1654 vs (C=O); 1623 vw, 1596 s (C=C). UV (hexane), λ_{max}/nm: 241, 250, 271, 280, 327, ~380. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.15 (t, 3 H, Me, J = 7.6 Hz); 2.63 (q, 2 H, CH_2, J = 7.6 Hz); 7.34 (s, 1 H, β-OH); 7.67, 7.75 (both td, 1 H each, H(6) and H(7), J_1 = 7.5 Hz, J_2 = 1.5 Hz); 8.07, 8.12 (both dd, 1 H each, H(8) and H(5), J_1 = 7.5 Hz, J_2 = 1.5 Hz). ^{1}H NMR (acetone-d_6), δ: 1.10

Scheme 2



2b—f **A** **B**

(t, 3 H, Me, J = 7.5 Hz); 2.58 (q, 2 H, CH_2, J = 7.5 Hz); 7.79, 7.85 (both td, 1 H each, H(6) and H(7), J_1 = 7.6 Hz, J_2 = 1.5 Hz); 8.04, 8.07 (both dd, 1 H each, H(8) and H(5), J_1 = 7.6 Hz, J_2 = 1.5 Hz); 9.48 (br.s, 1 H, β-OH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 12.6 (C(10)); 16.7 (C(9)); 125.9 (C(3)); 126.0 (C(8)); 126,7 (C(5)); 129.5 (C(8a)); 132.8 (C(7)); 133.0 (C(4a)); 134.8 (C(6)); 152.7 (C(2)); 181.5 (C(1)); 184.5 (C(4)). Mass spectrum, m/z (I_{rel} (%)): 203 $[M + 1]^+$ (20), 202 $[M]^+$ (100), 201 (22), 190 (17), 174 (11), 173 (13).

3-Ethyl-2,5-dihydroxy-1,4-naphthoquinone (2e) was synthesized by the ethylation of 2-hydroxyjuglone (**4b**). The yield was 133 mg (61%), R_f 0.37, m.p. 172—174 °C. IR (CCl_4), ν/cm^{-1}: 3397 m (β-OH); 1659 s, 1624 s (C=O); 1599 w, 1576 vw (C=C). UV (hexane), λ_{max}/nm: 205, 244, 370, 430, ~460. ^{1}H NMR (300 MHz, $CDCl_3$, 40 °C), δ: 1.16 (t, 3 H, Me, J = 7.6 Hz); 2.61 (q, 2 H, CH_2, J = 7.6 Hz); 7.27 (dd, 1 H, H(6), J_1 = 8.0 Hz, J_2 = 1.2 Hz); 7.41 (s, 1 H, C(2)OH); 7.52 (t, 1 H, H(7), J = 8.0 Hz); 7.63 (dd, 1 H, H(8), J_1 = 8.0 Hz, J_2 = 1.2 Hz); 12.49 (s, 1 H, C(5)OH). ^{13}C NMR (75 MHz, $CDCl_3$, 40 °C), δ: 12.6 (C(10)); 16.2 (C(9)); 114.6 (C(4a)); 119.1 (C(6)); 125.6 (C(3)); 126.2 (C(8)); 129.5 (C(8a)); 134.9 (C(7)); 153.4 (C(2)); 161.4 (C(5)); 180.8 (C(1)); 190.7 (C(4)). Mass spectrum, m/z (I_{rel} (%)): 220 $[M + 2]^+$ (5), 219 $[M + 1]^+$ (54), 218 $[M]^+$ (100), 190 (5), 175 (7).

3-Ethyl-2,8-dihydroxy-1,4-naphthoquinone (2f) was synthesized by the ethylation of 3-hydroxyjuglone (**4c**). The yield was 170 mg (78%), R_f 0.38, m.p. 140—143 °C. IR (CCl_4), ν/cm^{-1}: 3425 m (β-OH); 1654 m, 1628 sh.s (C=O); 1601 w, 1577 w (C=C). UV (hexane), λ_{max}/nm: ~220, ~245, 282, 413. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.14 (t, 3 H, Me, J = 7.6 Hz); 2.61 (q, 2 H, CH_2, J = 7.6 Hz); 7.18 (dd, 1 H, H(5), J_1 = 7.6 Hz, J_2 = 2.2 Hz); 7.23 (s, 1 H, C(2)OH); 7.60 (t, 1 H, H(6), J = 7.6 Hz); 7.64 (dd, 1 H, H(7), J_1 = 7.6 Hz, J_2 = 2.2 Hz); 11.07 (s, 1 H, α-OH). ^{13}C NMR (75 MHz, $CDCl_3$, 40 °C), δ: 12.5 (C(10)); 16.8 (C(9)); 113.0 (C(8a)); 119.6 (C(5)); 123.0 (C(7)); 127.3 (C(3)); 132.9 (C(4a)); 137.5 (C(6)); 152.4 (C(2)); 161.2 (C(8)); 183.6 (C(1)); 184.9 (C(4)). Mass spectrum, m/z (I_{rel} (%)): 219 $[M + 1]^+$ (22), 218 $[M]^+$ (100), 203 (9), 189 (11), 176 (11), 175 (33), 163 (7).

Oxidative coupling of hydroxyethylnaphthoquinones 2d—f. Freshly prepared PbO_2 (96 mg, 0.4 mmol)[17] was added with vigorous stirring to a solution of hydroxyethylnaphthoquinone **2d—f** (0.3 mmol) in glacial acetic acid (2 mL) heated to the boiling temperature. The reaction mixture was vigorously stirred for 3—5 min, cooled, and filtered. The filtrate was evaporated at temperatures <70 °C, and the residue was diluted with water (30 mL) and extracted with Et_2O (3×10 mL). The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*, and the resulting residue was chromatographed in hexane—acetone (4 : 1) and then benzene—hexane (2 : 1) systems.

3-(3-Ethyl-1,4-naphthoquinon-2-yloxy)-3-ethyl-2,3-dihydro-2-oxo-1,4-naphthoquinone (1c) was synthesized by the oxidative coupling of substrate **2d**. The yield was 109 mg (54%), R_f 0.27, m.p. 65—69 °C. Found (%): C, 71.38; H, 4.80. $C_{24}H_{18}O_6$. Calculated (%): C, 71.64; H, 4.51. IR ($CDCl_3$), ν/cm^{-1}: 1748 w, 1702 s, 1651 vs (C=O); ~1605 m, 1595 s, 1580 w (C=C). UV (hexane), λ_{max}/nm: 230, 250, 260, 280, 340, 390. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 1.08 (t, 3 H, Me, J = 7.5 Hz); 1.26 (t, 3 H, Me, J = 7.6 Hz); 2.13 (m, 2 H, CH_2); 2.84 (q, 2 H, CH_2, J = 7.6 Hz); 7.51 (td, 1 H, H(6′), J_1 = 7.6 Hz, J_2 = 1.3 Hz); 7.64 (m, 2 H, H(5′) and H(7′)); 7.93 (m, 2 H, H(6) and H(7)); 8.03 (dd, 1 H, H(8′), J_1 = 8.1 Hz, J_2 = 1.4 Hz); 8.22 (m, 1 H, H(5)); 8.41 (m, 1 H, (H8)). ^{13}C NMR (125 MHz), δ: 7.5 (C(10)); 12.4 (C(10′)); 17.5 (C(9′)); 31.0 (C(9)); 93.2 (C(3)); 126.2 (C(8′)); 126.5 (C(5′)); 128.4 (C(5)); 129.0 (C(8)); 130.6 (C(8′a)); 131.6 (C(4′a)); 132.9 (C(6′)); 133.0 (C(8a)); 134.0 (C(4a)); 134.4 (C(7′) and C(3′)); 134.8 (C(7)); 136.1 (C(6)); 150.8 (C(2′)); 180.6 (C(1)); 182.3 (C(4′)); 184.3 (C(2)); 184.2 (C(1′)); 189.1 (C(4)). Mass spectrum, m/z (I_{rel} (%)): 402 $[M]^+$ (12), 203 (22), 202 (100), 201 (57), 190 (19), 173 (24), 172 (31).

3-(3-Ethyl-5-hydroxy-1,4-naphthoquinon-2-yloxy)-3-ethyl-2,3-dihydro-5-hydroxy-2-oxo-1,4-naphthoquinone (1d) was synthesized by the oxidative coupling of substrate **2e**. The yield was 93 mg (43%), R_f 0.30, m.p. 80—85 °C. Found (%): C, 66.15; H, 4.42. $C_{24}H_{18}O_8$. Calculated (%): C, 66.36; H, 4.18. IR (CCl_4), ν/cm^{-1}: 1750 m, 1702 s, 1656 s, 1629 vs (C=O); 1598 m, 1578 w (C=C). UV (hexane), λ_{max}/nm: 265, 290, 369, 440, 480. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.08, 1.28 (both t, 3 H each, Me, J = 7.5 Hz); 2.16 (m, 2 H, CH_2); 2.82 (q, 2 H, CH_2, J = 7.5 Hz); 7.21 (dd, 1 H, H(6′), J_1 = 8.2 Hz, J_2 = 1.2 Hz); 7.26 (dd, 1 H, H(8′), J_1 = 7.5 Hz, J_2 = 1.2 Hz); 7.41 (t, 1 H, H(7′), J = 7.9 Hz); 7.46 (dd, 1 H, H(6), J_1 = 8.2 Hz, J_2 = 1.2 Hz); 7.79 (t, 1 H, H(7), J_1 = 7.9 Hz, J_2 = 8.2 Hz); 7.95 (dd, 1 H, H(8), J_1 = 1.3 Hz, J_2 = 7.5 Hz); 11.50, 12.26 (both s, 1 H each, α-OH). Mass spectrum, m/z (I_{rel} (%)): 435 $[M + 1]^+$ (5), 434 $[M]^+$ (14), 406 (2), 391 (3), 219 (17), 218 (100), 199 (8), 190 (9), 189 (10), 175 (38).

3-(3-Ethyl-8-hydroxy-1,4-naphthoquinon-2-yloxy)-3-ethyl-2,3-dihydro-8-hydroxy-2-oxo-1,4-naphthoquinone (1e) was synthesized by the oxidative coupling of substrate **2f**. The yield was 80 mg (37%), R_f 0.31, m.p. 187—192 °C. Found (%): C, 66.28; H, 4.25. $C_{24}H_{18}O_8$. Calculated (%): C, 66.36; H, 4.18. IR (CCl_4), ν/cm^{-1}: 1752 m, 1710 s, 1656 sh.s, 1628 vs (C=O); 1595 s, 1574 m (C=C). UV (ethanol), λ_{max}/nm: 230, 284, 400. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 1.08 (t, 3 H, Me, J = 7.5 Hz); 1.26 (t, 3 H, Me, J = 7.6 Hz); 2.14 (q, 2 H, CH_2, J = 7.5 Hz); 2.82 (q, 2 H, CH_2, J = 7.6 Hz); 7.08 (d, 1 H, H(7′), J_1 = 8.1 Hz); 7.44 (d, 1 H, H(7), J_1 = 8.1 Hz); 7.54 (t, 1 H, H(6′), J = 8.1 Hz); 7.62 (dd, 1 H, H(5′), J_1 = 7.6 Hz, J_2 = 1.2 Hz); 7.76 (dd, 1 H, H(5), J_1 = 7.6 Hz, J_2 = 1.2 Hz); 7.84 (t, 1 H, H(6), J = 8.1 Hz); 10.83, 11.89 (both s, 1 H each, C(8′)OH and C(8)OH). ^{13}C NMR (125 MHz), δ: 7.6 (C(10)); 12.3 (C(10′)); 17.7 (C(9′)); 31.4 (C(9)); 93.4 (C(3)); 114.1 (C(8′a)); 117.0 (C(8a)); 119.6 (C(5′)); 120.6 (C(5)); 124.0 (C(7′)); 124.7 (C(7)); 132.2 (C(4′a)); 134.0 (C(4a)); 135.9 (C(3′)); 137.3 (C(6′)); 139.0 (C(6)); 151.0 (C(2′)); 161.8 (C(8′)); 164.6 (C(8)); 183.2 (C(4′)); 184.4 (C(1)); 184.8 (C(2)); 186.5 (C(1′)); 188.3 (C(4)). Mass spectrum, m/z (I_{rel} (%)): 435 $[M + 1]^+$ (8), 434 $[M]^+$ (18), 433 $[M - 1]^+$ (9), 406 (24), 405 (19), 219 (17), 218 (100), 217 (85), 216 (10), 188 (18).

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