Reduction of 3-carbonyl-substituted 5,6-dicyanobenzofurans with sodium borohydride

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Reduction of 3-R-carbonyl-substituted 5,6-dicyanobenzofurans with sodium borohydride was studied under various conditions. 3-R-Carbonyl-substituted 5,6-dicyanobenzofurans are selectively reduced in ethanol to substituted 3-R-(hydroxymethyl)-5,6-dicyano-2-methylbenzofurans, products of more deep reduction, *viz.*, substituted 3-R-(hydroxymethyl)-2-methyl-2,3-dihydro-5,6-dicyanobenzofurans, 3-R-(hydroxymethyl)-5,6-dicyano-2-methylbenzofurans, and 3-alkyl-substituted 4-hydroxyphthalonitriles, are formed in tetrahydrofuran.

Key words: 3-R-carbonyl-substituted 5,6-dicyanobenzofurans, sodium borohydride, carbonyl group, 3-R-(hydroxymethyl)-5,6-dicyano-2-methylbenzofurans, 3-R-(hydroxymethyl)-5,6-dicyano-2-methyl-2,3-dihydrobenzofurans, stereo- and regioselective reduction, ^{1}H-^{1}H-correlation NOESY spectroscopy.

Pharmaceutical drugs of benzofuran series containing a keto group at position 3 are well known. Such medicines as Amiodarone, the third class antiarrhythmic, Benzbromarone and Benziodarone, medicines assisting in liberation of uric acid,[1] Benzofurocainum, the local anaesthetic,[2] Cloridarol, a vasodilator, whose carbonyl group at position 3 is substituted for the hydroxy one. Application of compounds of dihydrobenzofuran series in practical medicine is also described.[1] All this confirm actuality of the studies directed on the development of methods for the synthesis of new compounds of benzofuran series by the selective reduction of the carbonyl group.

It is known from the literature that a carbonyl group can be reduced with $NaBH_4$ to the corresponding alcohols in dioxane,[3] in acetic acid,[4] in alcohols,[5,6] with additives of cobalt, palladium, and lanthanide salts,[6,7] in alcohols in the presence of iodine,[8] $ZnCl_2$[9] in THF. Reductions of benzofuran ring to 2,3-dihydrobenzofuran with sodium amalgam or catalytically with hydrogen[10] are also described, but some of these methods require prolong heating and are accompanied by reduction of cyano groups.[6,8]

The purpose of the present work is to develop selective methods for the reduction of the carbonyl group in 3-R-carbonyl-substituted 5,6-dicyanobenzofurans with $NaBH_4$, with the cyano groups remaining intact and leading to the synthesis of 3-hydroxymethyl-substituted 5,6-dicyanobenzofurans earlier unreported in literature.

We studied reduction of 3-R-carbonyl-substituted 5,6-dicyano-2-methylbenzofurans[11] **1a—e** with $NaBH_4$ in EtOH and THF. It was found that the reduction of benzofurans **1a—d** in EtOH with a two-fold excess of $NaBH_4$ (20—25 °C, 30 min) leads to 3-R-(hydroxymethyl)-5,6-dicyano-2-methylbenzofurans **2a—d** in high yield (60—75%). Reduction of benzofurans **1a—d** in THF (20—25 °C, 2 h) is nonselective and leads to the mixtures of products with different extent of reduction: 3-R-(hydroxymethyl)-5,6-dicyano-2-methylbenzofurans **2a—d** (40—60%), 3-R-(hydroxymethyl)-5,6-dicyano-2-methyl-2,3-dihydrobenzofurans **3b—d** (20—40%), and 4-hydroxy-5-{1-[hydroxy-(4-R)methyl]propyl}phthalonitriles **4b—d** (Scheme 1). Compound **1a** was an exception, since no products of its deep reduction were isolated. In the case of compound **1d**, the reduction product **3d** was obtained in low yield (18%), whereas the corresponding phenol compound **4d** was detected in trace amounts.

It was found that treatment of benzofuran **1e** with $NaBH_4$ in EtOH and in THF does not lead to the reduction of the ester group to form the corresponding aliphatic alcohol.[9] Reduction in ethanol results in the benzofuran ring opening and leads to a mixture of *E*/*Z*-isomers of ethyl 2-(4,5-dicyano-2-hydroxyphenyl)but-2-enecarboxylate **5** (62%) in the ratio 2 : 3 (Scheme 2). The process in THF is more deep and results in the reduction of the double bond in butene **5** to yield ethyl 2-(4,5-dicyano-2-hydroxyphenyl)butanoate **6** (58%).

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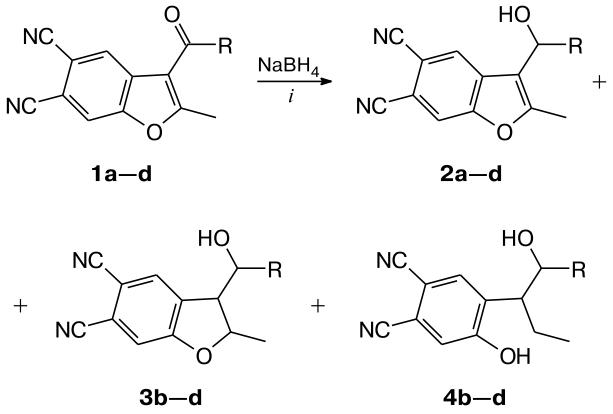
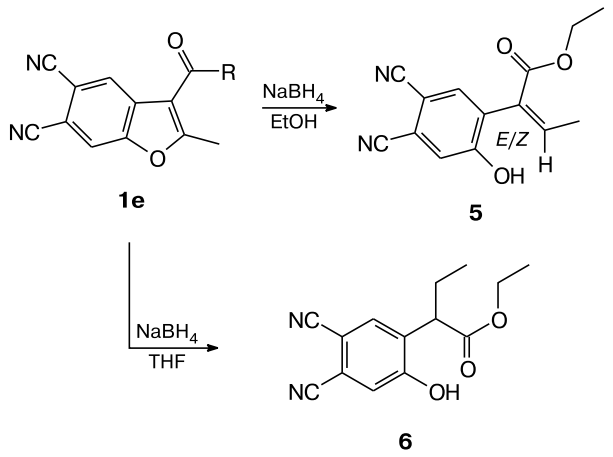
Scheme 1



1—4: R = Me (**a**), 4-C_6H_4OMe (**b**), 4-C_6H_4Me (**c**), 2-thienyl (**d**)

i. EtOH or THF.

Scheme 2



The structures of new compounds were confirmed by a combination of the IR and NMR spectroscopic and mass spectrometric data. It should be noted that not all the compounds gave a molecular ion, that is due to the instability of the compounds under electron impact.

The ^{1}H NMR data showed that formation of compounds **2** leads to the appearance of closely positioned signals for the OH and H(1′) protons in the region δ 5.0—6.5 as a pair of doublets with the common constant 4.0—4.5 Hz. For more accurate assignment of signals for the protons in compound **2a**, we recorded an ^{1}H-^{1}H-correlation NOESY spectrum. Analysis of the cross-peaks for the protons OH, H(1′), 2′-Me (the contacts with both one of the protons in the phthalonitrile ring and the protons of the 2-Me group are observed) allowed us to draw a conclusion that the OH group is at position 3 and to accurately assign the phthalonitrile protons.

For determination of *cis*- or *trans*-arrangement of protons in the furan ring, we recorded an ^{1}H-^{1}H correlation NOESY spectrum for compound **3b**. Analysis of the spectrum showed that there are no contacts between the 2-CH_3 protons and H(2″) and H(6″) protons of the phenyl substituent, whereas the cross-peaks between the H(2) and H(3) atoms have low intensity, that allows us to draw a conclusion on the *trans*-arrangement of these substituents. This agrees with the literature data[12,13] for similar compounds, whose constants have the following values J_{trans} 7 Hz and J_{cis} 8—9 Hz. It was found that reduction of the double bond is diastereoselective to yield only *trans*-isomer **3b—d** with the spin-spin coupling constant $J_{2,3}$ = 6.7—7.3 Hz.

We failed in separation of compound **5** to individual isomers by column chromatography. The ratio of isomers of compound **5** (*E*/*Z* 2/3) was determined from the integral intensities of a double set of signals in the ^{1}H NMR spectrum, assignments of signals were made based on the NOESY spectrum, which showed a correlation between the methyl proton at the double bond and the low-field hydroxyl proton in phthalonitrile.

The studies performed showed that 3-R-carbonyl-substituted 5,6-dicyanobenzofurans are selectively reduced with $NaBH_4$ in ethanol to the substituted 3-R-(hydroxymethyl)-5,6-dicyano-2-methylbenzofurans. In THF, in addition to the indicated target compounds, products of more deep reduction, *viz.*, *trans*-3-R-(hydroxymethyl)-5,6-dicyano-2-methyl-2,3-dihydrobenzofurans and 3-alkyl-substituted 4-hydroxyphthalonitriles are formed.

Experimental

IR spectra of suspensions in Nujol were recorded on a Perkin—Elmer RX-1 spectrometer with the wavelength 700—4000 cm^{-1}. Mass spectra were recorded on a FINNIGAN MAT INCOS 50 mass-spectrometer (70 eV). NMR spectra were recorded on a Bruker DRX-500 spectrometer for solutions in DMSO-d_6 at 30 °C. Signals for the residual protons in the solvents were references for the chemical shifts in the proton spectra ($\Delta\delta_H$ 2.50), signals for DMSO-d_6, in the carbon spectra ($\Delta\delta_C$ 39.5). The standard Bruker procedures were used for two-dimensional spectra. The time of mixing in the NOESY spectra was 0.3 s.

Synthesis of compounds 2a—d and 5 (general procedure). Sodium borohydride (0.0044 mol) was added to a suspension of compound **1** (0.002 mol) in EtOH (3 mL) and the mixture was stirred at 20—25 °C for 0.5 h, then it was poured into 1% aqueous HCl (10 mL). A resinous precipitate that formed was extracted with dichloromethane, the extract was thoroughly washed with water and subjected to chromatography on silica gel (eluent: hexane—ethyl acetate, 2 : 1). The eluent was evaporated, a precipitate was filtered off and recrystallized from EtOH.

Compound **5** was additionally purified by the acid-base reprecipitatation from water and isolated as a hydrate.

Synthesis of compounds 2a—d, 4a—d, and 6 (general procedure). Sodium borohydride (0.0044 mol) was added to a suspension of compound **1** (0.002 mol) in THF (3 mL) and the mixture was stirred at 20—25 °C for 2 h, then it was poured into 1% aq. HCl (10 mL). A resinous precipitate that formed was extracted

with dichloromethane, the extract was thoroughly washed with water. Individual compounds were separated by preparative column chromatography (silica gel was a stationary phase, hexane—ethyl acetate (2 : 1) was an eluent). The eluent was evaporated, a precipitate was filtered off and recrystallized from EtOH.

3-(1-Hydroxyethyl)-2-methyl-1-benzofuran-5,6-dicarbonitrile (2a). The yield was 67%, m.p. 134—136 °C (from ethanol). Found (%): C, 68.74; H, 4.20; N, 12.18. $C_{13}H_{10}N_2O_2$. Calculated (%): C, 69.02; H, 4.46; N, 12.38. IR (ν/cm^{-1}): 3199 (OH); 2233 (C≡N); 1613 (Ar); 1596; 1234 (C—O—C). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 226 [M^+] (27.4), 211 [M^+ – Me] (100), 181 [M^+ – MeCHOH] (14.7). ^{1}H NMR (DMSO-d$_6$), δ: 1.45 (d, 3 H, 2′-CH_3, J = 6.5 Hz); 2.54 (s, 3 H, 2-CH_3); 5.05 (dq, 1 H, H(1′), J = 3.8 Hz, J = 6.5 Hz); 5.40 (d, 1 H, OH, J = 3.8 Hz); 8.41 (s, 1 H, H(7)); 8.45 (s, 1 H, H(4)).

3-[Hydroxy(4-methoxyphenyl)methyl]-2-methyl-1-benzofuran-5,6-dicarbonitrile (2b). The yield was 76%, m.p. 139—141 °C. Found (%): C, 71.36; H, 4.22; N, 8.75. $C_{19}H_{14}N_2O_3$. Calculated (%): C, 71.69; H, 4.43; N, 8.80. IR (ν/cm^{-1}): 3491 (OH); 2232 (C≡N); 1612 (Ar); 1511; 1283 (C—O—C). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 318 [M^+] (10.5), 301 [M^+ – OH] (14.6), 209, 181 [M^+ – CHOH – 4-Me-C_6H_4] (18.6), 137 [$^+$CHOH – 4-Me-C_6H_4] (17.8), 109 (100). ^{1}H NMR (DMSO-d$_6$), δ: 2.58 (s, 3 H, CH_3); 3.72 (s, 3 H, OMe); 6.01 (d, 1 H, OH, J = 2.6 Hz); 6.07 (br.s, 1 H, CH); 6.89 (d, 2 H, H(3′), H(5′), J = 8.3 Hz); 7.38 (d, 2 H, H(2′), H(6′), J = 8.3 Hz); 8.19 (s, 1 H, H(4)); 8.42 (s, 1 H, H(7)).

3-[Hydroxy-(4-methylphenyl)methyl]-2-methyl-1-benzofuran-5,6-dicarbonitrile (2c). The yield was 68%, m.p. 150—152 °C (from ethanol). Found (%): C, 75.18; H, 4.46; N, 9.15. $C_{19}H_{14}N_2O_2$. Calculated (%): C, 75.48; H, 4.67; N, 9.27. IR (ν/cm^{-1}): 3490 (OH); 2224 (C≡N); 1611 (Ar); 1511 (Ar); 1273 (C—O—C). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 121 [CHOH – – 4-Me-$C_6H_4^+$] (100), 91 [4-Me-$C_6H_4^+$] (56.6). ^{1}H NMR (DMSO-d$_6$), δ: 2.26 (s, 3 H, 4′-CH_3); 2.58 (s, 3 H, 2-CH_3); 6.00 (d, 1 H, H(1′), J = 4.0 Hz); 6.09 (d, 1 H, OH, J = 4.0 Hz); 7.13 (d, 2 H, H(3′), H(5′), J = 7.7 Hz); 7.34 (d, 2 H, H(2′), H(6′), J = 7.7 Hz); 8.17 (s, 1 H, H(4)); 8.42 (s, 1 H, H(7)).

3-[Hydroxy(2-thienyl)methyl]-2-methyl-1-benzofuran-5,6-dicarbonitrile (2d). The yield was 62%, m.p. 115—117 °C (from ethanol). Found (%): C, 64.95; H, 3.40; N, 9.46. $C_{16}H_{10}N_2O_2S$. Calculated (%): C, 65.29; H, 3.42; N, 9.52. IR (ν/cm^{-1}): 3499 (OH); 2229 (C≡N); 1597 (Ar); 1284 (C—O—C). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 294 [M^+] (8.8), 277 [M^+ – OH] (7.6), 209 (12.7), 182 [M^+ – CHOH – C_4H_3S] (12.4), 111 (24.3), 85 (100). ^{1}H NMR (DMSO-d$_6$), δ: 2.60 (s, 3 H, CH_3); 6.31 (d, 1 H, H(1′), J = 4.4 Hz); 6.51 (d, 1 H, OH, J = 4.2 Hz); 6.96 (dd, 1 H, H(4′), J = 3.5 Hz, J = 5.0 Hz); 6.99 (d, 1 H, H(5′), J = 3.5 Hz); 7.44 (dd, 1 H, H(3′), J = 1.3 Hz, J = 5.0 Hz); 8.23 (s, 1 H, H(4)); 8.47 (s, 1 H, H(7)).

3-[Hydroxy(4-methoxyphenyl)methyl]-2-methyl-2,3-dihydro-1-benzofuran-5,6-dicarbonitrile (3b). The yield was 38%, m.p. 153—155 °C (from ethanol). Found (%): C, 70.95; H, 4.86; N, 8.59. $C_{19}H_{16}N_2O_3$. Calculated (%): C, 71.24; H, 5.03; N, 8.74. IR (ν/cm^{-1}): 3558 (OH), 2238 (C≡N); 1598 (Ar); 1253 (C—O—C). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 320 [M^+] (2.4), 209, 183 [M^+ – CHOH – 4-MeO-C_6H_4] (10.6), 137 [$^+$CHOH – – 4-MeO-C_6H_4] (100). ^{1}H NMR (DMSO-d$_6$), δ: 1.10 (d, 3 H, 2-CH_3, J = 6.4 Hz); 3.47 (dd, 1 H, H(3), J = 6.3 Hz, J = 7.3 Hz); 3.75 (s, 3 H, OCH_3); 4.70 (dd, 1 H, H(1′), J = 4.4 Hz, J = 7.3 Hz); 4.77 (qd, 1 H, H(2), J = 6.4 Hz, J = 6.3 Hz); 5.77 (d, 1 H, OH, J = 4.4 Hz); 6.91 (d, 2 H, H(3′), H(5′), J = 8.7 Hz); 7.26 (d, 2 H, H(2′), H(6′), J = 8.7 Hz); 7.50 (s, 1 H, H(7)); 7.70 (s, 1 H, H(4)).

3-[Hydroxy(4-methylphenyl)methyl]-2-methyl-2,3-dihydro-1-benzofuran-5,6-dicarbonitrile (3c). The yield was 28%, m.p. 147—149 °C (from ethanol). Found (%): C, 74.69; H, 5.06; N, 8.91. $C_{19}H_{16}N_2O_2$. Calculated (%): C, 74.98; H, 5.30; N, 9.20. IR (ν/cm^{-1}): 3550 (OH); 2231 (C≡N); 1596 (Ar); 1257 (C—O—C). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 121 [CHOH – 4-Me-$C_6H_4^+$] (100), 91 [4-Me-$C_6H_4^+$] (46.2). ^{1}H NMR (DMSO-d$_6$), δ: 1.09 (d, 3 H, 2-CH_3, J = 6.3 Hz); 2.30 (s, 3 H, 4′-CH_3); 3.48 (dd, 1 H, H(3), J = 6.3 Hz, J = 7.0 Hz); 4.72 (dd, 1 H, H(1′), J = 4.5 Hz, J = 7.0 Hz); 4.78 (quint, 1 H, H(2), J = 6.3 Hz); 5.85 (d, 1 H, OH, J = 4.5 Hz); 7.16 (d, 2 H, H(3′), H(5′), J = 8.0 Hz); 7.22 (d, 2 H, H(2′), H(6′), J = 8.0 Hz); 7.53 (s, 1 H, H(7)); 7.68 (s, 1 H, H(4)). ^{13}C NMR (DMSO-d$_6$), δ: 20.74 (4′-Me); 20.96 (2-Me); 55.10 (C(3)); 73.47 (C(1″)); 84.09 (C(2)); 105.56 (C(5)); 114.54 (C(7)); 115.49 (C≡N); 116.00 (C≡N); 115.62 (C(6)); 126.73 (C(2′), C(6′)); 128.77 (C(3′)/C(5′)); 131.76 (C(4)); 135.79 (C(3a)); 136.78 (C(4′)); 138.99 (C(1′)); 162.96 (C(7a)).

3-[Hydroxy(2-thienyl)methyl]-2-methyl-2,3-dihydro-1-benzofuran-5,6-dicarbonitrile (3d). The yield was 18%, m.p. 143—146 °C (from ethanol). Found (%): C, 64.58; H, 3.89; N, 9.34. $C_{16}H_{12}N_2O_2S$. Calculated (%):C, 64.85; H, 4.08; N, 9.45. IR (ν/cm^{-1}): 3560 (OH); 2220 (C≡N); 1244 (C—O—C). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 296 [M^+] (14.8), 184 [M^+ – CH – – OH – C_4H_3S] (24.4), 169 [M(184)$^+$ – Me] (40.9), 113 [CH – – OH – $C_4H_3S^+$] (100). ^{1}H NMR (DMSO-d$_6$), δ: 1.20 (d, 3 H, CH_3, J = 6.4 Hz); 3.53 (dd, 1 H, H(3), J = 6.4 Hz, J = 6.7 Hz); 4.89 (quint, 1 H, H(2), J = 6.4 Hz); 5.10 (dd, 1 H, H(1′), J = 4.5 Hz, J = 6.7 Hz); 6.34 (d, 1 H, OH, J = 4.5 Hz); 6.31 (br.d, 1 H, H(1′), J = 4.2 Hz); 6.51 (d, 1 H, OH, J = 4.2 Hz); 6.94 (br.d, 1 H, H(5′), J = 3.5 Hz); 6.99 (dd, 1 H, H(4′), J = 3.5 Hz, J = 5.0 Hz); 7.47 (dd, 1 H, H(5′), J = 1.2 Hz, J = 5.0 Hz); 7.55 (s, 1 H, H(4)), 7.74 (s, 1 H, H(7)). ^{13}C NMR (DMSO-d$_6$), δ: 11.74; 13.82; 23.76; 45.66; 60.32; 104.04; 114.34: 115.67: 116.31; 119.65; 132.54; 134.62; 159,43; 171.88.

4-Hydroxy-5-{1-[hydroxy(4-methoxyphenyl)methyl]propyl}-phthalonitrile (4b). The yield was 28%, m.p. 233—235 °C (from ethanol). Found (%): C, 66.95; H, 5.72; N, 8.20. $C_{19}H_{18}N_2O_3 \cdot \cdot H_2O$. Calculated (%): C, 67.05; H, 5.92; N, 8.23. IR (ν/cm^{-1}): 3562 (OH); 2321 (C≡N); 1590, 1618 (Ar). ^{1}H NMR (DMSO-d$_6$), δ: 0.61 (t, 3 H, CH_3, J = 7.4 Hz); 1.46, 1.52 (both ddq, 1 H each, CH_2, J = 7.4 Hz, J = 13.8 Hz, J = 7.4 Hz); 3.28 (br.m, 1 H, C<u>H</u>CH_2); 3.78 (s, 3 H, 4′-OCH_3); 4.80 (d, 1 H, CHO, J = 7.4 Hz); 5.35 (br.s, 1 H, OH); 6.97 (d, 2 H, H(3′), H(5′), J = 8.5 Hz); 7.21 (d, 2 H, H(2′), H(6′), J = 8.5 Hz); 7.30 (s, 1 H, H(3)); 7.96 (s, 1 H, H(6)); 11.29 (br.s, 1 H, 4-OH).

4-Hydroxy-5-{1-[hydroxy(4-methylphenyl)methyl]propyl}-phthalonitrile (4c). The yield was 38%, m.p. 240—242 °C (from ethanol). Found (%): C, 70.19; H, 5.97; N, 8.41. $C_{19}H_{18}N_2O_2 \cdot \cdot H_2O$. Calculated (%): C, 70.35; H, 6.21; N, 8.64. IR (ν/cm^{-1}): 3560 (OH); 2320 (C≡N); 1592, 1610 (Ar). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 121 [CHOH – 4-Me-$C_6H_4^+$] (100), 91 [4-Me-$C_6H_4^+$] (49.0). ^{1}H NMR (DMSO-d$_6$), δ: 0.59 (t, 3 H, CH_3, J = 7.4 Hz); 1.44, 1.50 (both ddq, 1 H each, CH_2, J = 7.4 Hz, J = 13.8 Hz, J = 7.4 Hz); 2.26 (s, 3 H, 4′-CH_3); 3.27 (br.s, 1 H, C<u>H</u>CH_2); 4.81 (d, 1 H, CHO, J = 7.3 Hz); 5.37 (br.s, 1 H, OH); 7.07 (d, 2 H, H(3′), H(5′), J = 8.1 Hz); 7.11 (d, 2 H, H(2′), H(6′), J = 8.1 Hz); 7.28 (s, 1 H, H(3)); 7.92 (s, 1 H, H(6)); 11.25 (br.s, 1 H, 4-OH). ^{13}C NMR (DMSO-d$_6$), δ: 11.93 (1′-CH_3);

21.08 (4″-CH_3); 24.43 (C(2′)); 47.30 (C(3′)); 74.62 (C(4′)); 103.97 (C(1)); 113.11 (C(2)); 116.45 (C≡N); 117.24 (C≡N); 119.27 (C(3)); 126.80 (C(2″)/C(6″)); 128.71 (C(3″)/C(5″)); 135.57 (C(5)); 136.19 (C(6)); 137.18 (C(1″)); 141.79 (C(4″)); 160.79 (C(4)).

A mixture of *E*/*Z*-isomers 5 in the ratio 2 : 3. The yield was 62%, m.p. 124—126 °C (from hexane). Found (%): C, 61.13; H, 5.02; N, 10.15. $C_{14}H_{12}N_2O_3 \cdot H_2O$. Calculated (%): C, 61.31; H, 5.14; N, 10.21. MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 256 [M^+] (8.7), 210 [M^+ – OEt] (91.3), 195 [M^+ – OEt – Me] (47.8), 181 [M^+ – OEt – Me – OH] (100).

Ethyl (2*Z*)-2-(4,5-dicyano-2-hydroxyphenyl)but-2-enecarboxylate (*Z*-5). ^{1}H NMR (DMSO-d_6), δ: 1.15 (t, 3 H, CH_3, J = 7.1 Hz); 2.05 (d, 3 H, 4-CH_3, J = 7.2 Hz); 4.13 (q, 2 H, CH_2, J = 7.1 Hz); 6.45 (q, 1 H, H(3), J = 7.2 Hz); 7.3 (s, 1 H, H(3′)); 7.91 (s, 1 H, H(6′)); 11.75 (s, 1 H, OH).

Ethyl (2*E*)-2-(4,5-dicyano-2-hydroxyphenyl)but-2-enecarboxylate (*E*-5). ^{1}H NMR (DMSO-d_6), δ: 1.16 (t, 3 H, CH_3, J = 7.1 Hz); 1.66 (d, 3 H, 4-CH_3, J = 7.2 Hz); 4.11 (q, 2 H, CH_2, J = 7.1 Hz); 7.13 (q, 1 H, H(3), J = 7.2 Hz); 7.4 (s, 1 H, H(3′)); 7.83 (s, 1 H, H(6′)); 11.75 (s, 1 H, OH).

Ethyl 2-(4,5-dicyano-2-hydroxyphenyl)butanoate (6). The yield was 58%, m.p. 160—162 °C (from hexane). Found (%): C, 60.68; H, 5.72; N, 10.01. $C_{14}H_{14}N_2O_3 \cdot H_2O$. Calculated (%): C, 60.86; H, 5.84; N, 10.14. IR (ν/cm^{-1}): 3546 (OH); 2233 (C≡N); 1598, 1615 (Ar). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 258 [M^+] (39.5), 212 [$M^+ - C_2H_5OH$] (100), 184 [$M^+ - C_2H_5OH$ – Et] (81), 169 (34), 157 (98), 141 (22), 102 (25), 76 (10). ^{1}H NMR (DMSO-d_6), δ: 0.80 (d, 3 H, 4-CH_3, J = 7.4 Hz); 1.12 (d, 3 H, $OCH_2\underline{CH}_3$, J = 7.1 Hz); 1.77 (ddq, 1 H, 3-CH_2, J = 7.5 Hz, J = 14.1 Hz, J = 7.4 Hz); 1.98 (ddq, 1 H, 3-CH_2, J = 7.5 Hz, J = 14.1 Hz, J = 7.4 Hz); 3.82 (t, 1 H, H(2), J = 7.4 Hz, J = 7.5 Hz); 4.06 (q, 2 H, OCH_2, J = 7.1 Hz); 7.33 (s, 1 H, H(3′)); 7.87 (s, 1 H, H(6′)); 11.74 (s, 1 H, OH).

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