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Synthesis of 8-Aroylpyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-triones and Their Reaction with Water. New Analogs of Cyclic Dipeptides

A. V. Chervyakov[a], P. A. Slepukhin[b], M. V. Dmitriev[a], and A. N. Maslivets[a]

[a] *Perm State National Research University, ul. Bukireva 15, Perm, 614990 Russia*
e-mail: koh2@psu.ru

[b] *Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia*

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Abstract—2-Aryl-8-aroyl-3,4-dihydropyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-triones prepared from (*Z*)-1-aryl-3-(2-aryl-2-oxoethylidene)piperazin-2-ones and oxalyl chloride react with water to afford (*E*)-8a-hydroxy-2-aryl-8-[aryl(hydroxy)methylene]tetrahydropyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-triones. The crystal and molecular structure of 8-benzoyl-2-phenyl-3,4-dihydropyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-trione and (*E*)-8a-hydroxy-8-[hydroxy(phenyl)methylene]-2-phenyltetrahydropyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-trione were studied by X-ray diffraction analysis.

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Heterocyclic enaminoketones reacting with oxalyl chloride afford hetareno[*e*]pyrrole-2,3-diones [1–4] or 4-heterylfuran-2,3-diones [4, 5]. In order to extend the range of data providing a possibility to predict the occurrence of one or another of these two routes we synthesized (*Z*)-1-aryl-3-(2-aryl-2-oxoethylidene)piperazin-2-ones **1a–1c** and investigated their reactions with oxalyl chloride.

Piperazinones **1a–1c** were prepared from methyl 4-aryl-2-hydroxy-4-oxobut-2-enoates and *N*-arylethylenediamines in toluene in the presence of catalytic quantities of glacial acetic acid by boiling for 1 h. The use of toluene as solvent made it possible to reduce the reaction time and slightly increase the yield of target products as compared with the known procedure of piperazinone **1c** synthesis in ethanol [6].

Compounds **1a–1c** are light-yellow high melting crystalline substances readily soluble in DMF and DMSO, sparingly soluble in ethanol, benzene, toluene, insoluble in water and alkanes.

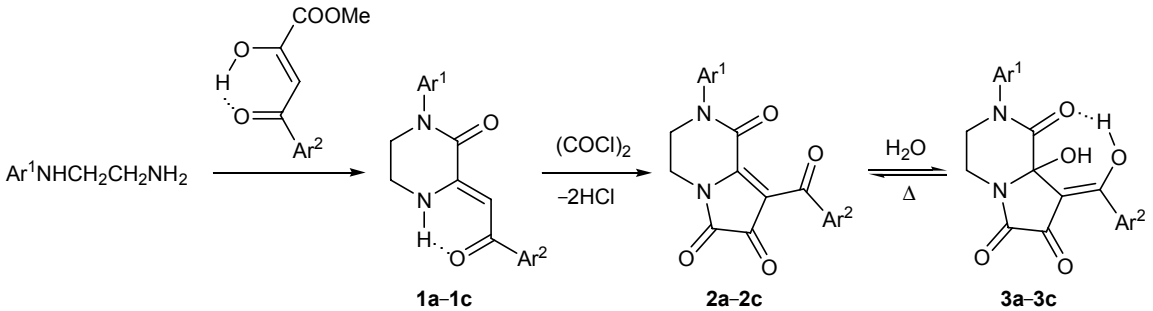
IR spectra of compounds **1a–1c** contain the bands of the stretching vibrations of the NH group as a broad band in the region 3150–3214 cm^{-1}, of lactam carbonyl group (1668–1671 cm^{-1}), and aroyl carbonyl group (1603–1607 cm^{-1}) involved in the formation of an intramolecular hydrogen bond.

In ^{1}H NMR spectra of compounds **1a–1c** along with the signals of aromatic protons and the protons of the methyl group (for compound **1b**) two multiplets appear of the protons of two methylene groups in the region 3.69–3.97 ppm, a singlet from the proton of vinyl group CH (6.57–6.63 ppm), and a broadened singlet in the downfield region 10.86–10.88 ppm from the proton of NH group involved in the formation of the intramolecular hydrogen bond.

The spectral characteristics of compounds **1a–1c** show that they exist in the crystalline state and in solutions with a strong intramolecular hydrogen bond of H-chelate type between the NH group and the aroyl group, i.e. in the form of *Z*-isomers characteristic of the compounds of this class [6].

The reactions of compounds **1a–1c** with oxalyl chloride in toluene (1 h at room temperature and 2–2.5 h of boiling till the end of HCl liberation under the common conditions for the synthesis of five-membered dioxoheterocycles [7]) furnished instead of expected 4-heterylfuran-2,3-diones 2-aryl-8-aroyl-3,4-dihydropyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-triones **2a–2c**, [8], whose structure was confirmed by XRD analysis by an example of compound **2a**.

Pyrrolopyrazinetriones **2a–2c** are bright red high melting crystalline substances readily soluble in DMF



$Ar^1 = Ar^2 = Ph$ (**a**); $Ar^1 = C_6H_4Me$-4, $Ar^2 = Ph$ (**b**); $Ar^1 = Ph$, $Ar^2 = C_6H_4Cl$-4 (**c**).

and DMSO, sparingly soluble in chloroform, benzene, toluene, insoluble in alkanes; they react with water and alcohols and quickly suffer discoloration at storage due to the reaction with the air moisture.

In the IR spectra of compounds **2a–2c** the bands of stretching vibration are present of lactam C^6=O (1754–1755 cm^{-1}), C^1=O (1663–1691 cm^{-1}), ketone C^7=O (1721–1731 cm^{-1}) and aroyl (1614–1665 cm^{-1}) carbonyl groups. The higher wave number corresponding to the band of stretching vibrations of lactam group compared to the band of ketone group is in agreement with the published data on these groups in the IR spectra of substituted furan-2,3-diones [9] and isatins [10].

In ^{1}H NMR spectra of compounds **2a–2c** solutions along with the signals of aromatic protons a three-proton singlet appears from the protons of the methyl group at 2.28 ppm (in the spectrum of compound **2b**), and two multiplets of protons from two methylene groups in the region 3.75–4.13 ppm.

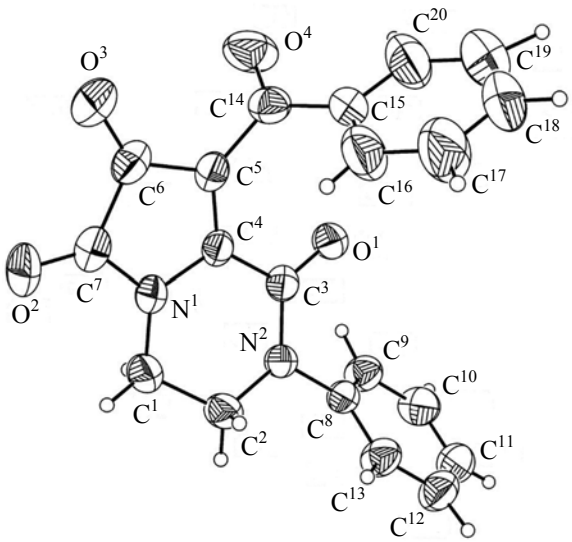


Fig. 1. Molecular structure of 8-benzoyl-2-phenyl-3,4-dihydropyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-trione **2a**.

According to XRD data on compound **2a** (Fig. 1), the five-membered heterocycle of the heterobicyclic system is flat, and the six-membered ring is present in the *pseudo-sofa* conformation. The benzoyl fragment is virtually planar and turned at a considerable angle with respect to the plane of the heterobicyclic system.

As known, 4-acyl-substituted 1*H*-pyrrole-2,3-diones and hetareno[*e*]pyrrole-2,3-diones {3-acylpyrrolo[2,1-*c*][1,4]benzoxazine-1,2,4-triones and {3-acylpyrrolo[1,2-*a*]quinoxaline-1,2,4(5*H*)-triones} may reversibly add OH-nucleophiles (water and alcohol) to the carbon atom in the position *5* of the 1*H*-pyrrole-2,3-dione ring giving the corresponding 4-acyl-3,5-dihydroxy- and 5-alkoxy-4-acyl-3-hydroxy-2,5-dihydro-1*H*-pyrrol-2-ones [7].

At keeping 2-aryl-8-aroyl-3,4-dihydropyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-triones **2a–2c** in toluene saturated with water for 8–12 h (till discoloration) we obtained (*E*)-2-aryl-8-[aryl(hydroxy)methylene]-8a-hydroxytetrahydropyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-triones **3a–3c**, whose structure was confirmed by XRD analysis by an example of compound **3b**.

Compounds **3a–3c** are light-yellow crystalline substances melting with decomposition, readily soluble in DMF and DMSO, sparingly soluble in chloroform, benzene, toluene, insoluble in alkanes and water. The light yellow solutions of compounds **3a–3c** in glacial acetic acid or DMSO at heating become bright red, and the intensity of color grows proportionally to the growing temperature, apparently due to the reversibility of water addition to pyrrolopyrazine-triones **2**.

The IR spectra of compounds **3a–3c** contain the bands of the stretching vibrations of the alcohol group C^{8a}OH as a narrow peak in the region 3185–3290 cm^{-1}, of enol group C^8=C(Ar)OH involved in the formation of the intramolecular hydrogen bond as a broad peak in

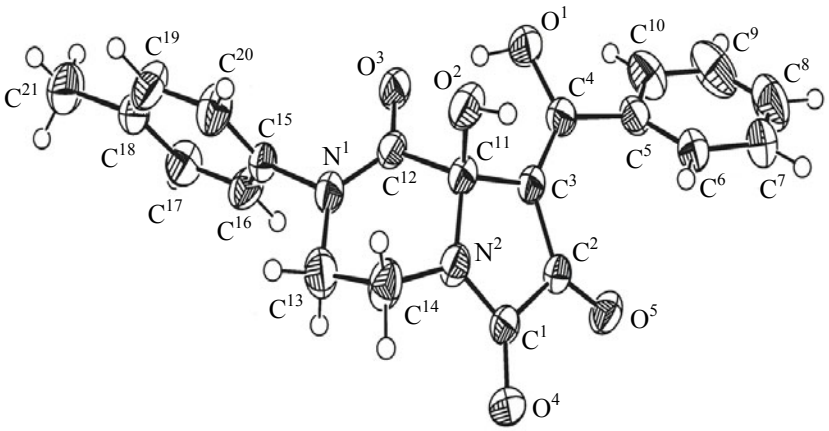


Fig. 2. Molecular structure of (*E*)-8a-hydroxy-8-[hydroxy(phenyl)methylidene]-2-(4-tolyl)tetrahydropyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-trione **3b**.

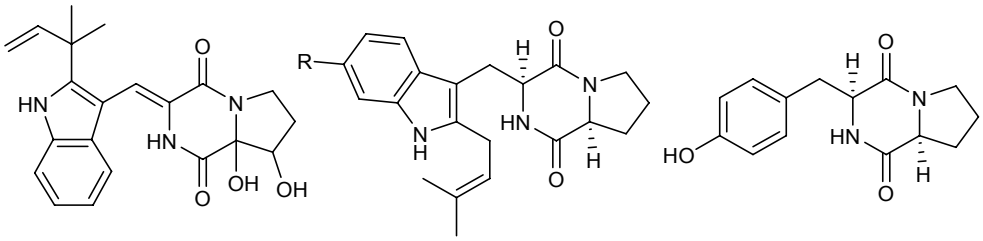
the region 3064–3079 cm^{-1}, of carbonyl groups C^6=O, C^7=O of the pyrroledione ring (1693–1723 cm^{-1}), and of lactam carbonyl group C^1=O (1585–1603 cm^{-1}) involved in the formation of the intramolecular hydrogen bond.

In ^{1}H NMR spectra of compounds **3a–3c** along with the signals of aromatic protons two doublets of doublets are present belonging to four protons of two methylene groups in the region 3.90–4.11 ppm, a broadened singlet of the proton of the alcohol group C^{8a}OH in the region 7.31–7.38 ppm, and a three- proton singlet of the methyl group at 2.28 ppm (in the spectrum of compound **3b**) are observed. The signal of enol group C^8=C(Ar)OH involved in the formation of the intramolecular hydrogen bond is strongly broadened (9–13 ppm) and is not seen in the spectrum.

According to XRD data compound **3b** crystallized in a centrosymmetric space group in the form of a hydrate in a ratio 1 : 2 (Fig. 2). The heterobicyclic system is not planar, it is bent along the axis C^{11}–C^{14}. The enol hydroxy group forms a strong intramolecular hydrogen bond with the lactam carbonyl group C^{12}=O^3. The tolyl substituent is disordered by two positions with approximately 0.5 occupancy; it may be described as the ring rotation around the C^{15}–C^{18} axis (this disordering is not shown in Fig. 2). The water molecules are also disordered by two positions with equal occupancy. The molecules in the crystal form an infinite two-dimensional net parallel to the [0 0 1] plane due to the developed system of intermolecular hydrogen bonds involving the groups O^2–H^2, C^1=O^4, C^2=O^5 and water molecules.

Pyrrolopyrazinetriones **2a–2c** react with water adding OH groups to the carbon atom in the position *5* of the 1*H*-pyrrole-2,3-dione ring as has been previously observed with 4-acyl-substituted 1*H*-pyrrole-2,3-diones [7], yet in the addition products **3a–3c** the proton is located not at the oxygen atom of the carbonyl group in the position *3* of the 1*H*-pyrrole-2,3-dione ring, but at the oxygen atom of the aroyl group followed by the formation of the intramolecular hydrogen bond of this group with the oxygen atom of the carbonyl group in the position *1* of the pyrrolopyrazinetriones.

The heating in capillary of compounds **3a–3c** to the temperatures close to the melting point (130–140°C) led to water elimination and the formation of initial pyrrolopyrazinetriones **2a–2c**.



Brevianamide U Tryprostatins Maculosin

Thus we developed a new method of synthesis of functionalized heterobicyclic system of pyrrolo[1,2-*a*]-pyrazine, analog of 2,5-diketopiperazine, the smallest of known cyclic peptides. The natural 2,5-diketopiperazines (brevianamides [11], tryprostatins [12], maculosin [13], etc.), as well as synthetic *N*-substituted pyrrolopyrazines exhibit antitumor, phytotoxic, and other kinds of activity [14].

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Perkin Elmer Spectrum Two from mulls in mineral oil or in perfluorinated oil. ^{1}H NMR spectra were registered on a spectrometer Bruker Avance III (operating frequency 500 MHz), internal reference TMS. Elemental analysis was carried out on an analyzer vario MICRO cube. The homogeneity of compounds synthesized was confirmed by TLC (Silufol plates, eluents benzene–ethyl acetate, 5 : 1, ethyl acetate, development in iodine vapor), the optimization of the reaction conditions and registration of mass spectra were performed by procedure ultra-HPLC-MS, column Acquity UPLC C18 1.7 μm, mobile phase acetonitrile–water, flow rate 0.3–0.6 mL/min, detector ESI MS Xevo TQD, electrospray ionization in the mode of positive ions registration ESI$^+$, temperature 150°C, voltage on the capillary 3500 V, on the cone 50 V.

(*Z*)-3-(2-Oxo-2-phenylethylidene)-1-phenyl-piperazin-2-one (1a). To 15.0 g (72.7 mmol) of methyl 4-aryl-2-hydroxy-4-oxobut-2-enoate in a mixture of 100 mL of toluene and 40 mL of glacial acetic acid was added 9.5 mL (72.7 mmol) of *N*-phenylethylenediamine, and the reaction mixture was boiled for 1 h (TLC monitoring), evaporated to 40 mL volume, the precipitate was filtered off. Yield 92%, mp 154–156°C (toluene). IR spectrum, ν, cm^{-1}: 3214 br (NH in intramolecular hydrogen bond), 1671 (C^2=O), 1607 br (COPh). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.70 m (2H, C^{5}H$_2$), 3.97 m (2H, C^{6}H$_2$), 6.60 s (1H, C^3=CH), 7.31 m (1H$_{arom}$), 7.42–7.56 group of signals (7H$_{arom}$), 7.89 d (2H, H^o in COPh, *J* 6.8 Hz), 10.86 s (1H, NH). Found, %: C 73.83; H 5.38; N 9.65. $C_{18}H_{16}N_2O_2$. Calculated, %: C 73.95; H 5.52; N 9.58.

Compounds **1b** and **1c** were synthesized similarly.

(*Z*)-3-(2-Oxo-2-phenylethylidene)-1-(4-tolyl)piperazin-2-one (1b). Yield 89%, mp 177–178°C (toluene). IR spectrum, ν, cm^{-1}: 3150 br (NH in intramolecular hydrogen bond), 1670 (C^2=O), 1605 br (COPh). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.31 s (3H, Me), 3.69 m (2H, C^{5}H$_2$), 3.91 m (2H, C^{6}H$_2$), 6.63 s (1H, C^3=CH), 7.23 d (2H, H^m in C$_6$H$_4$Me-4, *J* 8.4 Hz), 7.31 d (2H, H^o in C$_6$H$_4$Me-4, *J* 8.4 Hz), 7.50 m (3H$_{arom}$), 7.90 d (2H, H^o in COPh, *J* 7.0 Hz), 10.88 s (1H, NH). Found, %: C 74.35; H 5.95; N 9.20. $C_{19}H_{18}N_2O_2$. Calculated, %: C 74.49; H 5.92; N 9.14.

(*Z*)-3-[2-Oxo-2-(4-chlorophenyl)ethylidene]-1-phenylpiperazin-2-one (1c). Yield 80%, mp 201–202°C (toluene). IR spectrum, ν, cm^{-1}: 3213 br (NH in intramolecular hydrogen bond), 1668 (C^2=O), 1603 br (COC$_6$H$_4$). ^{1}H NMR spectrum [(CD$_3$)$_2$CO)], δ, ppm: 3.67 m (2H, C^{5}H$_2$), 3.97 m (2H, C^{6}H$_2$), 6.57 s (1H, C^3=CH), 7.31 m (1H$_{arom}$), 7.41–7.45 m (4H$_{arom}$), 7.54 d (2H, H^m in COC$_6$H$_4$Cl-4, *J* 8.5 Hz), 7.90 d (2H, H^o in COC$_6$H$_4$Cl-4, *J* 8.5 Hz), 10.88 s (1H, NH). Found, %: C 66.00; H 4.71; N 8.53. $C_{18}H_{15}ClN_2O_2$. Calculated, %: C 66.16; H 4.63; N 8.57.

8-Benzoyl-2-phenyl-3,4-dihydropyrrolo[1,2-*a*]-pyrazine-1,6,7(2*H*)-trione (2a). To a solution of 5.0 g (17.1 mmol) of piperazinone **1a** in 250 mL of anhydrous toluene was added 2.2 mL (25.7 mmol) of oxalyl chloride, the mixture was maintained for 1 h, boiled for 2 h, and cooled. The solvent was distilled off in a vacuum on a rotary evaporator. Yield 90%, mp 150–151°C (toluene). IR spectrum, ν, cm^{-1}: 1755 (C^6=O), 1731 (C^7=O), 1663 (C^1=O), 1650 (COPh). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 4.02 d.d (2H, C^{4}H$_2$, *J* 6.8, 4.2 Hz), 4.13 d.d (2H, C^{3}H$_2$, *J* 6.8, 4.2 Hz), 7.24–7.50 group of signals (7H$_{arom}$), 7.57 t (1H$_{arom}$), 7.87 d (2H, H^o in COPh, *J* 7.3 Hz). Found, %: C 69.42; H 4.09; N 8.03. $C_{20}H_{14}N_2O_4$. Calculated, %: C 69.36; H 4.07; N 8.09.

Compounds **2b** and **2c** were synthesized similarly.

8-Benzoyl-2-(4-tolyl)-3,4-dihydropyrrolo[1,2-*a*]-pyrazine-1,6,7(2*H*)-trione (2b). Yield 70%, mp 147–148°C (toluene). IR spectrum, ν, cm^{-1}: 1755 (C^6=O), 1726 (C^7=O), 1672 (C^1=O), 1660 (COPh). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 2.30 s (3H, Me), 3.75–4.05 group of signals (4H, CH$_2$CH$_2$), 7.07–7.87 group of signals (9H$_{arom}$). Found, %: C 70.09; H 4.42; N 7.74. $C_{21}H_{16}N_2O_4$. Calculated, %: C 69.99; H 4.48; N 7.77.

2-Phenyl-8-(4-chlorobenzoyl)-3,4-dihydropyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-trione (2c). Yield 77%, mp 147–149°C (toluene). IR spectrum, ν, cm^{-1}: 1755 (C^6=O), 1721 (C^7=O), 1691 (C^1=O), 1665 (COC$_6$H$_4$). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm:

3.83 m (2H, C^4H_2), 4.04 m (2H, C^3H_2), 7.20–7.39 m (5H, Ph), 7.50 d (2H, H^m in COC_6H_4Cl-4, *J* 8.5 Hz), 7.96 d (2H, H^o in COC_6H_4Cl-4, *J* 8.5 Hz). Found, %: C 63.24; H 3.30; N 7.34. $C_{20}H_{13}ClN_2O_4$. Calculated, %: C 63.09; H 3.44; N 7.36.

(*E*)-8a-Hydroxy-8-[hydroxy(phenyl)methylidene]-2-phenyltetrahydropyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-trione (3a). A beaker with a solution of 0.50 g (1.40 mmol) of pyrrolopyrazinetrione **2a** in 20 mL of toluene and a beaker with 50 mL of heated to boiling water were placed in a vacuum desiccator, the air was pumped out, and the desiccator was left standing for 12 h. Yield 95%, mp 147–149°C (decomp., toluene). IR spectrum, ν, cm^{-1}: 3290 ($C^{8a}\underline{OH}$), 3078 br (C^8=C$\underline{OH}$), 1723 (C^6=O), 1698 (C^7=O), 1603 br (C^1=O in intramolecular hydrogen bond). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.90 d.d (2H, C^4H_2, *J* 6.5, 4.6 Hz), 4.11 d.d (2H, C^3H_2, *J* 6.5, 4.6 Hz), 7.29 t ($1H_{arom}$), 7.33 d.d ($2H_{arom}$), 7.35 s (1H, C^{8a}OH), 7.39–7.43 m ($2H_{arom}$), 7.50 t ($2H_{arom}$), 7.63 t ($1H_{arom}$), 8.00 d (2H, H^o in COPh, *J* 8.2 Hz). Found, %: C 65.80; H 4.38; N 7.80. $C_{20}H_{16}N_2O_5$. Calculated, %: C 65.93; H 4.43; N 7.69.

Compounds **3b, 3c** were synthesized similarly.

(*E*)-8a-Hydroxy-8-[hydroxy(phenyl)methylidene]-2-(4-tolyl)tetrahydropyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-trione (3b). Yield 93%, mp 149–151°C (decomp., toluene). IR spectrum, ν, cm^{-1}: 3450–3050 (2OH), 1720 (C^6=O), 1698 (C^7=O), 1585 br (C^1=O in intramolecular hydrogen bond). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.33 s (3H, Me), 4.02 d.d (2H, C^4H_2, *J* 3.8, 6.6 Hz), 4.10 d.d (2H, C^3H_2, *J* 3.8, 6.6 Hz), 7.13–7.24 group of signals ($4H_{arom}$), 7.31 s (1H, C^{8a}OH), 7.44 t ($2H_{arom}$), 7.57 t ($1H_{arom}$), 7.86 d [2H, H^o in C(OH)Ph, *J* 8.3 Hz]. Mass spectrum: *m/z* 379.11 [M + H]$^+$. Found, %: C 66.72; H 4.68; N 7.31. $C_{21}H_{18}N_2O_5$. Calculated, %: C 66.66; H 4.80; N 7.40. *M* 379.13.

(*E*)-8a-Hydroxy-8-[hydroxy(4-chlorophenyl)methylidene]-2-phenyltetrahydropyrrolo[1,2-*a*]pyrazine-1,6,7(2*H*)-trione (3c). Yield 88%, mp 153–155°C (decomp., toluene). IR spectrum, ν, cm^{-1}: 3185 ($C^{8a}\underline{OH}$), 3064 br (C^8=C$\underline{OH}$), 1693 (C^6=O, C^7=O), 1597 br (C^1=O in intramolecular hydrogen bond). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.00 d.d (2H, C^4H_2, *J* 6.5, 4.2 Hz), 4.10 d.d (2H, C^3H_2, *J* 6.5, 4.2 Hz), 7.24–7.41 m (5H, Ph), 7.38 s (1H, C^{8a}OH), 7.39 d (2H, H^m in C_6H_4Cl-4, *J* 8.4 Hz), 7.77 d (2H, H^o in C_6H_4Cl-4, *J* 8.4 Hz). Found, %: C 60.39; H 3.66; N 6.89. $C_{20}H_{15}ClN_2O_5$. Calculated, %: C 60.24; H 3.79; N 7.02.

X-ray diffraction study. Unit cell parameters and the array of experimental reflections of single crystals of compound **2a** and **3b** were measured on automatic four-circle diffractometers with CCD-detectors Xcalibur S (**2a**) and Xcalibur R (**3b**) by the method of ω-2θ-scanning with a monochromatized MoK_α-radiation at 295(2) K. The structures were solved by the direct statistical method and refined by full-matrix least-squares method with respect to F^2 in anisotropic approximation for all nonhydrogen atoms. A part of hydrogen atoms was placed in geometrically calculated positions and was included in the refinement in a *rider* model with thermal parameters depending on parent atoms; another part of hydrogen atoms was solved and refined independently in an isotropic approximation. All calculations were performed using SHELX 97 software [15].

The analysis of compound **2a** (empirical formula $C_{20}H_{14}N_2O_4$) was carried out using colorless crystal of the size 0.25 × 0.17 × 0.09 mm. Crystal triclinic, space group P-1, *a* 5.9760(6), *b* 11.8515(11), *c* 13.5823(8) Å, α 100.406(7), β 90.771(7), γ 95.331(8) deg, *V* 941.60(14) Å^3, d_{calc} 1.222 g/cm^3, *Z* 2. In the angles range 3.05 < θ < 28.28° 4618 independent reflections were measured, 1875 with $I > 2\sigma(I)$. The completeness of the experiment for the angle θ 28.28° was 99.3%. No corrections for extinction were introduced (μ 0.087 mm^{-1}). Final refinement results were as follows: R_1 0.0451, wR_2 0.1205 for reflections with $I > 2\sigma(I)$, R_1 0.0968, wR_2 0.1260 (for all reflections), *S* 1.001. Maximum and minimum peaks of residual electron density are 0.156 and –0.182 ē Å^{-3}.

The analysis of compound **3b** (empirical formula $C_{21}H_{18}N_2O_5 \cdot 2H_2O$) was carried out using yellow crystal of the size 0.60 × 0.40 × 0.40 mm, grown from the toluene saturated with water. Crystal triclinic, space group P-1, *a* 8.8608(10), *b* 8.9181(10), *c* 13.9454(15) Å, α 87.661(9), β 73.676(10), γ 72.816(10)°, *V* 1009.28(19) Å^3, d_{calc} 1.364 g/cm^3, *Z* 2. In the angles range 2.99 < θ < 29.65° 4778 independent reflections were measured, 3810 with $I > 2\sigma(I)$. The completeness of the experiment for the angle θ < 26.00° was 99.6%. The extinction was accounted for empirically using the algorithm SCALE3 ABSPACK [16]. Final refinement results were as follows: R_1 0.0474, wR_2 0.1218 for reflections with $I > 2\sigma(I)$, R_1 0.0602, wR_2 0.1289 for all reflections, *S* 1.077. Maximum and minimum peaks of residual electron density are 0.274 and –0.226 ē Å^{-3}.

The results of structural experiments are deposited in the Cambridge Crystallographic Data Center under the numbers CCDC 1437902 and CCDC 1438227. The data may be obtained free at the address www.ccdc.cam.ac.uk.

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