SYNTHESIS AND BACTERICIDAL ACTIVITY OF 6-*H*(NITRO)-9-ARYLIDENEDEOXYVASICINONES AND THEIR PERCHLORATES

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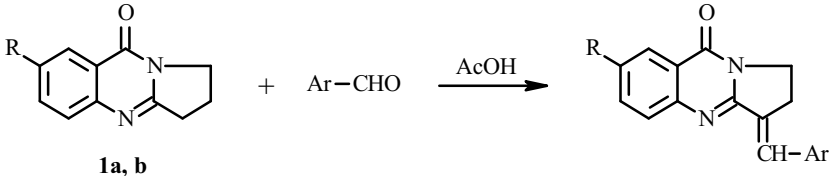
9-Arylidene-6H(nitro)deoxyvasicinones were synthesized by reaction of 6H(nitro)deoxyvasicinones and aromatic aldehydes and furfurol in glacial acetic acid.

Key words: deoxyvasicinone, aldehydes, condensation, bactericidal properties.

We have previously studied the condensation of deoxyvasicinone (**1a**) with several aromatic, aliphatic, and unsaturated aldehydes by fusion of a mixture of the reagents [1]. It was found that the reaction occurs only with aromatic and heterocyclic aldehydes. Aliphatic and unsaturated aldehydes do not react with **1a**. The direction of the reaction depends on the nature of the substituent in the aromatic ring of the aldehyde and the conditions. Thus, whereas *m*- and *p*-nitrobenzaldehydes form under realtively mild conditions 9-α-hydroxybenzyl-**1a**, higher temperatures and other aromatic aldehydes give 9-arylidene-deoxyvascinones. In contrast with this, condensation of **1a** and 6-bromo-**1a** (R = Br) in glacial acetic acid with aromatic aldehydes proceeds more smoothly and gives exclusively 9-arylidenedeoxyvasicinones (R = H, Br) [2-4]. It is known that 9-α-hydroxy(*m*- and *p*-nitro)benzyldeoxyvasicinones lose water under more forcing conditions and transform into 9-(*m*- and *p*-nitro)benzylidene-**1a** [1].

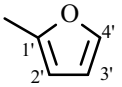
We studied the reaction of **1a** with 3,4-dimethoxybenzaldehyde, isovanillin, 2-bromoisovanillin, 5-bromovanillin, and furfurol in glacial acetic acid in order to expand this condensation to other aldehydes and to seek potential biologically active compounds.

We reacted 6-nitrodeoxyvasicinone (**1b**, R = NO_2) with aromatic aldehydes in order to explain the effect of the substituent on the aromatic ring on the reactivity and compared the results with those for 6-*H*(bromo)deoxyvasicinones (**1**, R = H, Br) [5]. As it turned out, the electron-accepting nitro group, like bromine, had a positive effect, i.e., enhances formation of the condensation products. Reactions of **1b**, like for 6-*H*(bromo)deoxyvasicinones (**1**, R = H, Br) [2-4], were carried out by refluxing equimolar amounts of a mixture of the reagents in glacial acetic acid for 3-5 h. Target compounds **3a-i** were obtained in good yields.



1a, b **2a - e** **3a - i**

2a: R = H, Ar = $C_6H_3(OCH_3)_2$-3,4
2b: R = H, Ar = $C_6H_3(OH)(OCH_3)$-3,4
2c: R = H, Ar = $C_6H_2(Br)(OH)(OCH_3)$-2,3,4
2d: R = H, Ar = $C_6H_2(OCH_3)(OH)(Br)$-3,4,5
3a: R = NO_2, Ar = C_6H_5
3b: R = NO_2, Ar = C_6H_4OH-4
3c: R = NO_2, Ar = $C_6H_4N(CH_3)_2$-4
3d: R = NO_2, Ar = $C_6H_4NO_2$-4
3e: R = NO_2, Ar = $C_6H_3(OCH_3)_2$-3,4
3f: R = NO_2, Ar = $C_6H_2(Br)(OH)(OCH_3)$-2,3,4
3g: R = NO_2, Ar = $C_6H_2(OCH_3)(OH)(Br)$-3,4,5
3h: R = NO_2, Ar = $C_6H_2(OCH_3)(OH)(Br)$-3,4,6
2e: R = H; **3i:** R = NO_2

2e, 3i: Ar = 

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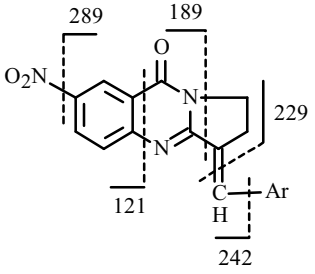
The reaction of **1b** with aldehydes, like for 6-*H*(bromo)deoxyvasicinones (**1**, R = H, Br), occurred through formation of intermediate 9-hydroxyarylmethylquinazolin-4-ones. However, these compounds were not observed in our experiments.

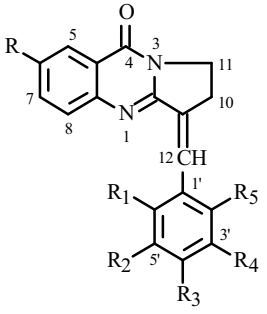
It is known that perchlorates of arylidene derivatives of bicyclic quinazolines possess bacteriocidal activity [6]. We prepared perchlorates (**4a-i**) in high yields (68-99%) in order to seek potential bacteriocides. The reactions were carried out with heating of a mixture of reagents in acetic acid in the presence of conc. $HClO_4$.

The structures of **2a-e** and **3a-i** were confirmed by IR, PMR, and mass spectra. Their IR spectra contained $\nu_{C=O}$ stretching vibrations at 1650-1710 cm^{-1}; $\nu_{C=N}$, at 1580-1610 cm^{-1}; ν_{C-N}, at 1540-1557 cm^{-1}; ν_{C-NO_2}, at 1510 cm^{-1}.

The synthesized compounds fragmented mainly by the following scheme (**3b** as an example):



3b



2a - e
3a - i

2a - e: R = H; **3a - i:** R = NO_2

Methylene protons in the β-position had chemical shfits (CS) in the PMR spectrum of 3.13-3.26 ppm (2H, triplet); in the γ-position, of 4.15-4.29 ppm (2H, triplet). $N(CH_3)_2$– methyl protons of **3c** had CS at 3.07 ppm (6H, singlet); OCH_3 of **3f** and **3g**, 3.64 and 3.61 ppm (3H, singlet). Aromatic protons appeared at 6.72-8.86 ppm. Protons of β- and γ-methylenes were observed as triplets, which confirmed that the condensation occurred at the α-carbon atom.

We studied the bacteriocidal properties of the synthesized compounds in various concentrations (0.01, 0.1, 1%) for various gram-positive and gram-negative strains: *Staphylococcus* T50a, *Klebsiella pneumoniae* T3a, *S. aureus* T48a, *Acinetobacter sp.* T16, *Enterococcus hormaechei* T2, *Escherichia coli* T60a, *En. hormaechei* T10, *Proteus rettgerri* T33a, *B. Cereus* T80, *Citrobacter freundii* T1a, *En. faecalis* T23a, *Pseudomonas aureginosa* T31a, *Pr. agglomerans* T26, *A. faecalis* T3, *Micrococcus luteus* T52a, *P. aureginosa* T145, *S. saprophyticus* T415, *K. oxitoca* T4a, and *A. haumanii* T15a. The results showed that they possessed moderate (**3a**, **3f**, **3i**) and low (**2a-e**, **3b-e**, **3g**, **3h**, **4a-i**) bacteriocidal properties.

EXPERIMENTAL

Mass spectra were recorded on a MS-30 instrument (Kratos); IR spectra, in mineral oil on a System 2000 IR-Fourier spectrometer; PMR spectra, in TFA on a Unity 400+ instrument (operating frequency 400 MHz, TMS internal standard, δ scale). The purity of products and course of reactions were monitored by TLC on Silufol UV-254 plates using benzene:methanol (3:1, system A; 5:1, system B) and $CHCl_3$:CH_3OH (20:1, system C).

Deoxyvasicinone (**1a**) was prepared by the literature method [7].

6-Nitrodeoxyvasicinone (**1b**) was synthesized by a modified method [8].

6-Nitrodeoxyvasicinone (1b). Deoxyvasicinone (**1a**, 12 g, 0.06 mol) was treated with cooling (0-2°C) with conc. H_2SO_4 (24 mL, 95.72%, ρ = 1.835 g/cm^3), stirred at 0-2°C, treated dropwise with a nitrating mixture consisting of nitric (9 mL, 59.69%, ρ = 1.365 g/cm^3) and sulfuric (ρ = 1.835 g/cm^3) acids. The reaction mixture was stirred at room temperature for 2 h and poured into ice. The resulting precipitate was filtered off, washed with water until the rinsings were neutral, and dried. Recrystallization from methanol afforded **1b** (12.2 g, 82%), mp 188-189°C, which agreed with the literature [8].

9-(3′,4′-Dimethoxybenzylidene)deoxyvasicinone (2a). A mixture of **1a** (0.3 g, 1.6 mmol) and 3,4-dimethoxybenzaldehyde (0.24 g, 1.7 mmol) in glacial acetic acid (5 mL) was refluxed for 3-5 h. The solvent was distilled off. The solid was recrystallized from aqueous DMF to afford **2a** (0.39 g, 72%), $C_{20}H_{18}O_3N_2$, mp 212-214°C (aq. DMF), R_f 0.65 (system B).

PMR spectrum (δ, ppm, J/Hz): 8.08 (1H, d, J = 8.04, H-5), 7.72 (1H, td, J = 8.3, H-7), 7.65 (1H, s, H-2′), 7.62 (1H, d, J = 8.3, H-6′), 7.39 (1H, t, J = 7.3, H-6), 7.19 (1H, br.s, H-12), 7.18 (1H, d, J = 7.3, H-5′), 7.02 (1H, d, J = 7.8, H-8), 4.15 (2H, t, J = 6.8, H-11), 3.56 [6H, d, $(OCH_3)_2$], 3.25 (2H, br.t, J = 7.8, H-10).

9-(3′-Hydroxy-4′-methoxybenzylidene)deoxyvasicinone (2b) was synthesized analogously as above from **1a** (0.3 g, 1.6 mmol) and isovanillin (0.25 g, 1.7 mmol) to afford **2b** (0.45 g, 93%), $C_{19}H_{16}O_3N_2$, mp 212-214°C (aq. DMF), R_f 0.51 (system A).

PMR spectrum (δ, ppm, J/Hz): 8.85 (1H, s, OH), 8.07 (1H, d, J = 7.8, H-5), 7.71 (1H, td, J = 8.03, H-7), 7.63 (1H, s, H-2′), 7.62 (1H, d, J = 8.03, H-6′), 7.38 (1H, t, J = 7.56, H-6), 7.1 (1H, br.s, H-12), 7.06 (1H, d, J = 8.7, H-8), 6.6 (1H, d, J = 8.26, H-5′), 4.18 (2H, t, J = 7.56, H-11), 3.78 (3H, s, OCH_3), 3.18 (2H, t, J = 6.61, H-10).

9-(2′-Bromo-3′-hydroxy-4′-methoxybenzylidene)deoxyvasicinone (2c) was synthesized analogously as above from **1a** (0.3 g, 1.6 mmol) and 2-bromoisovanillin (0.39 g, 1.7 mmol) to afford **2c** (0.62 g, 96%), $C_{19}H_{15}O_3N_2Br$, mp 232-234°C (aq. DMF), R_f 0.38 (system B).

PMR spectrum (δ, ppm, J/Hz): 7.98 (1H, d, J = 7.84, H-5), 7.92 (1H, br.s, H-12), 7.61 (1H, t, J = 7.47, H-7), 7.39 (1H, d, J = 7.85, H-8), 7.36 (1H, br.t, J = 8.22, H-6), 6.92 (1H, d, J = 8.9, H-6′), 6.63 (1H, br.d, J = 8.6, H-5′), 4.15 (2H, t, H-11), 3.57 (3H, s, OCH_3), 3.1 (2H, br.t, H-10).

Mass spectrum (*m/z*, %): 398/400 (8) $[M]^+$, 319 (100) $[M - Br]^+$, 304 (47), 303 (68), 247 (22), 204 (6), 196 (3.5), 184 (5) $[M - CHAr]^+$, 160 (17.5).

9-(3′-Methoxy-4′-hydroxy-5′-bromobenzylidene)deoxyvasicinone (2d) was synthesized analogously as above from **1a** (0.3 g, 1.6 mmol) and 5-bromovanillin (0.39 g, 1.7 mmol) to afford **2d** (0.57 g, 88%), $C_{19}H_{15}O_3N_2Br$, mp 222-224°C (aq. DMF), R_f 0.52 (system A).

PMR spectrum (δ, ppm, J/Hz): 8.08 (1H, d, J = 8.2, H-5), 7.65 (1H, t, J = 7.5, H-7), 7.58 (1H, br.s, H-12), 7.43 (1H, t, J = 8.2, H-6), 7.38 (1H, d, J = 7.8, H-8), 7.11 (1H, s, H-6′), 6.74 (1H, s, H-2′), 4.25 (2H, t, H-11), 3.6 (3H, s, OCH_3), 3.17 (2H, br.t, H-10).

9-(Furfurylidene-2)deoxyvasicinone (2e) was synthesized analogously as above from **1a** (0.3 g, 1.6 mmol) and furfurol (0.14 mL, 0.16 g, 1.7 mmol, ρ = 1.1598 g/cm^3) to afford **2e** (0.29 g, 70%), $C_{16}H_{12}O_2N_2$, mp 234°C (lit. [1] mp 228°C) (aq. DMF), R_f 0.74 (system B).

PMR spectrum (δ, ppm, J/Hz): 8.07 (1H, dd, J = 1.4, 7.8, H-5), 7.72 (1H, td, J = 1.4, 7.08, H-7), 7.61 (1H, d, J = 8.2, H-8), 7.48 (1H, t, J = 5.7, H-6), 7.39 (1H, br.s, H-12), 7.37 (1H, d, J = 1.18, H-4′), 6.81 (1H, d, J = 3.55, H-2′), 6.61 (1H, dd, J = 1.65, 3.31, H-3′), 4.3 (2H, t, J = 7.09, H-11), 3.18 (2H, td, J = 2.8, 10.15, H-10).

6-Nitro-9-benzylidenedeoxyvasicinone (3a). A mixture of **1b** (0.5 g, 2.16 mmol) was dissolved in glacial acetic acid (5 mL), treated with benzaldehyde (0.23 mL, 0.24 g, 2.3 mmol, ρ = 1.0498 g/cm^3), refluxed for 3-5 h, and left overnight. Solvent was distilled off. The solid was recrystallized from benzene to afford **3a** (0.48 g, 70%), $C_{18}H_{13}O_3N_3$, mp 258-259°C, R_f 0.72 (system A).

PMR spectrum (δ, ppm, J/Hz): 8.85 (1H, d, J = 2.2, H-5), 8.41 (1H, dd, J = 9.0, 2.5, H-7), 7.82 (1H, br.s, H-12), 7.65 (1H, d, J = 9.0, H-8), 7.10-7.27 (5H, m, H-2′,3′,4′,5′,6′), 4.25 (2H, t, J = 7.6, H-11), 3.20 (2H, t, J = 6.4, H-10).

Mass spectrum (*m/z*, %): 319 (50.0) $[M]^+$, 273 (10.5) $[M - NO_2]^+$, 242 (4.2) $[M - Ar]^+$, $[M - 1]^+$ (100), 288 (44), 272 (35), 243 (38), 215 (7), 170 (7).

6-Nitro-9-benzylidenedeoxyvasicinone Perchlorate (4a). 6-Nitro-9-benzylidenedeoxyvasicinone (**3a**, 12 mg, 0.037 mmol) was dissolved with heating in glacial acetic acid (3 mL), treated with perchloric acid (2 drops, 58%, ρ = 1.512 g/cm^3), heated for 10 min, and left overnight. The resulting crystals were filtered off, washed with water and alcohol, and dried to afford **4a** perchlorate (15 mg, 95%), $C_{18}H_{14}O_7N_3Cl$, mp 233-235°C (dec.).

Perchlorates **4b-i** were synthesized analogously.

6-Nitro-9-(4′-hydroxybenzylidene)deoxyvasicinone (3b) was synthesized analogously as above from **1b** (0.5 g, 2.16 mmol) and 4-hydroxybenzaldehyde (0.26 g, 2.16 mmol) to afford **3b** (0.47 g, 65%), $C_{18}H_{13}O_4N_3$, mp 306°C (dec.), R_f 0.68 (system A).

PMR spectrum (δ, ppm, J/Hz): 8.82 (1H, d, J = 2.3, H-5), 8.38 (1H, dd, J = 2.6, 9.0, H-7), 7.76 (1H, br.s, H-12), 7.62 (1H, d, J = 9.0, H-8), 7.26 (1H, d, J = 8.6, H-5′), 7.26 (1H, d, J = 8.6, H-3′), 6.72 (1H, d, J = 8.6, H-6′), 6.72 (1H, d, J = 8.6, H-2′), 4.24 (2H, t, H-11), 3.15 (2H, br.t, H-10).

Mass spectrum (*m/z*, %): 335 (65) $[M]^+$, 289 (2.8) $[M - NO_2]^+$, 242 (10.5) $[M - Ar]^+$, 229 (3.5) $[M - (CH - Ar)]^+$, $[M - 1]^+$ (100), 288 (52), 202 (4.2), 170 (2.8), 144 (12.6).

Perchlorate of 3b (4b): $C_{18}H_{14}O_8N_3Cl$, yield 99%, mp 235°C (dec.).

6-Nitro-9-(4′-dimethylaminobenzylidene)deoxyvasicinone (3c) was synthesized analogously as above from **1b** (0.5 g, 1.95 mmol) and 4-dimethylaminobenzaldehyde (0.32 g, 2.2 mmol) to afford **3c** (0.36 g, 46%), $C_{20}H_{18}O_3N_4$, mp 280°C (dec. aq. DMF), R_f 0.69 (system B).

PMR spectrum (δ, ppm, J/Hz): 8.85 (1H, d, J = 2.3, H-5), 8.43 (1H, dd, J = 2.4, 9.0, H-7), 7.87 (1H, br.s, H-12), 7.72 (1H, d, J = 9.0, H-8), 7.52 (1H, d, J = 9.0, H-5′), 7.52 (1H, d, J = 9.0, H-3′), 7.42 (1H, d, J = 9.0, H-2′), 7.42 (1H, d, J = 9.0, H-6′), 4.27 (2H, t, J = 7.2, H-11), 3.20 (2H, br.t, H-10), 3.07 [6H, s, $N(CH_3)_2$].

Mass spectrum (*m*/*z*, %): 362 (100) $[M]^+$, 316 (26) $[M - NO_2]^+$, 242 (9) $[M - Ar]^+$, 332 (41), 315 (90), 300 (28.7), 272 (16.8), 243 (12), 215 (2), 158 (12.6).

Perchlorate of 3c (4c): $C_{20}H_{19}O_7N_4Cl$, yield 99%, mp 242-244°C (dec.).

6-Nitro-9-(4′-nitrobenzylidene)deoxyvasicinone (3d) was synthesized analogously as above from **1b** (0.5 g, 2.16 mmol) and 4-nitrobenzaldehyde (0.33 g, 2.16 mmol) to afford **3d** (0.54 g, 69%), $C_{18}H_{12}O_5N_4$, mp 308-310°C (aq. DMF), R_f 0.91 (system C).

PMR spectrum (δ, ppm, J/Hz): 8.86 (1H, d, J = 2.0, H-5), 8.43 (1H, dd, J = 2.4, H-7), 8.03 (1H, d, J = 9.0, H-5′), 8.03 (1H, d, J = 9.0, H-3′), 7.92 (1H, br.s, H-12), 7.7 (1H, d, J = 9.4, H-8), 7.47 (1H, d, J = 8.6, H-6′), 7.47 (1H, d, J = 8.6, H-2′), 4.29 (2H, t, J = 6.8, H-11), 3.23 (2H, br.t, H-10).

Mass spectrum (*m*/*z*, %): 364 (53) $[M]^+$, 318 (15.4) $[M - NO_2]^+$, 242 (16.8) $[M - Ar]^+$, 229 (5.6) $[M - (CH - Ar)]^+$, 363 (100), 334 (20), 317 (50), 271 (33), 231 (14.7), 216 (18), 202 (6), 182 (6.3).

Perchlorate of 3d (4d): $C_{18}H_{13}O_9N_4Cl$, yield 86%, mp 270°C (dec.).

6-Nitro-9-(3′,4′-dimethoxybenzylidene)deoxyvasicinone (3e) was synthesized analogously as above from **1b** (0.5 g, 2.16 mmol) and 3,4-dimethoxybenzaldehyde (0.35 g, 2.16 mmol) to afford **3e** (0.64 g, 78%), $C_{20}H_{17}O_5N_3$, mp 229-230°C (aq. DMF), R_f 0.78 (system A).

PMR spectrum (δ, ppm, J/Hz): 8.83 (1H, d, J = 2.5, H-5), 8.39 (1H, dd, J = 2.2, 8.9, H-7), 7.77 (1H, br.s, H-12), 7.64 (1H, d, J = 9.0, H-8), 7.05 (1H, d, J = 8.7, H-5′), 6.87 (1H, s, H-2′), 6.76 (1H, d, J = 8.4, H-6′), 4.26 (2H, t, J = 7.2, H-11), 3.60, 3.61 [6H, d, $(OCH_3)_2$], 3.19 (2H, t, H-10).

Mass spectrum (*m*/*z*, %): 379 (100) $[M]^+$, 333 (11.2) $[M - NO_2]^+$, 229 (1.4) $[M - (CH - Ar)]^+$, 378 (23), 356 (22.3), 332 (14.7), 291 (7), 245 (2), 200 (11.2), 173 (4.2), 151 (12), 146 (4.8).

Perchlorate of 3e (4e): $C_{20}H_{18}O_9N_3Cl$, yield 68%, mp 262-264°C (dec.).

6-Nitro-9-(2′-bromo-3′-hydroxy-4′-methoxybenzylidene)deoxyvasicinone (3f) was synthesized from **1b** (0.4 g, 1.7 mmol) and 2-bromoisovanillin (0.4 g, 1.7 mmol) to afford **3f** (0.6 g, 86%), $C_{19}H_{14}O_5N_3Br$, mp 298-299°C (aq. DMF), R_f 0.76 (system B).

PMR spectrum (δ, ppm, J/Hz): 8.85 (1H, d, J = 2.3, H-5), 8.4 (1H, dd, J = 2.2, 9.0, H-7), 8.09 (1H, br.s, H-12), 7.65 (1H, d, J = 9.0, H-8), 7.05 (1H, d, J = 8.8, H-5′), 6.7 (1H, d, J = 8.8, H-6′), 4.2 (2H, t, H-11), 3.64 (3H, s, OCH_3), 3.13 (2H, t, H-10).

Mass spectrum (*m*/*z*, %): 443/446 (4.2) $[M]^+$, 241/244 (3.5) $[M - Ar]^+$, 229 (1.4) $[M - (CH - Ar)]^+$, 362/365 (100), 332/335 (12.6), 318 (80), 302/305 (32), 273/276 (7.7), 244/247 (5.6), 216/219 (4.8), 182 (3.5), 142 (3.5).

Perchlorate of 3f (4f): $C_{19}H_{15}O_9N_3BrCl$, yield 79%, mp 224°C (dec.).

6-Nitro-9-(3′-methoxy-4′-hydroxy-5′-bromobenzylidene)deoxyvasicinone (3g) was synthesized analogously as above from **1b** (0.4 g, 1.7 mmol) and 5-bromovanillin (0.4 g, 1.7 mmol) to afford **3g** (0.39 g, 52%), $C_{19}H_{14}O_5N_3Br$, mp 293-294°C (aq. DMF), R_f 0.78 (system B).

PMR spectrum (δ, ppm, J/Hz): 8.83 (1H, d, J = 2.6, H-5), 8.39 (1H, dd, J = 2.3, 8.8, H-7), 7.70 (1H, br.s, H-12), 7.66 (1H, d, J = 9.1, H-8), 7.15 (1H, s, J = 2.0, H-2′), 6.76 (1H, d, J = 2.0, H-6′), 4.26 (2H, t, J = 6.8, H-11), 3.61 (3H, s, OCH_3), 3.18 (2H, t, H-10).

Mass spectrum (*m*/*z*, %): 443/446 (100) $[M]^+$, 398 (2.1) $[M - NO_2]^+$, 241/244 (3.5) $[M - Ar]^+$, 229 (2.8) $[M - (CH - Ar)]^+$, 413/416 (10), 335 (8.4), 319/322 (11.2), 302/305 (6.3), 273/276 (3.5), 244/247 (10.5), 215 (9), 144 (3).

Perchlorate of 3g (4g): $C_{19}H_{15}O_9N_3BrCl$, yield 69%, mp 300°C (dec.).

6-Nitro-9-(3′-hydroxy-4′-methoxy-6′-bromobenzylidene)deoxyvasicinone (3h) was synthesized analogously as above from **1b** (0.3 g, 1.3 mmol) and 6-bromoisovanillin (0.3 g, 1.3 mmol) to afford **3h** (0.33 g, 58%), $C_{19}H_{14}O_5N_3Br$, mp 288-289°C (aq. DMF), R_f 0.76 (system B).

PMR spectrum (δ, ppm, J/Hz): 8.84 (1H, d, J = 2.7, H-5), 8.4 (1H, dd, J = 2.4, 9.0, H-7), 8.07 (1H, br.s, H-12), 7.65 (1H, d, J = 9.0, H-8), 6.97 (1H, s, H-5′), 6.88 (1H, s, H-2′), 4.26 (2H, t, H-11), 3.6 (3H, s, OCH_3), 3.19 (2H, t, H-10).

Mass spectrum (*m*/*z*, %): 444 (2.4) $[M]^+$, 241/244 (5.6) $[M - Ar]^+$, 229 (1.5) $[M - (CH - Ar)]^+$, 378 (92), 332/335 (100), 315/318 (23), 303/306 (16.8), 287/290 (19.6), 273/276 (10.5), 259/262 (10), 216 (5), 174 (5), 145 (8).

Perchlorate of 3h (4h): $C_{19}H_{15}O_9N_3BrCl$, yield 72%, mp 238-240°C (dec.).

6-Nitro-9-(furfurylidene-1′)deoxyvasicinone (3i) was synthesized analogously as above from **1b** (0.5 g, 2.16 mmol) and furfurol (0.18 mL, 0.2 g, 2.17 mmol, ρ = 1.1598 g/cm^3) to afford **3i** (0.52 g, 78%), $C_{16}H_{11}O_4N_3$, mp 240°C (dec., benzene), R_f 0.72 (system B).

PMR spectrum (δ, ppm, J/Hz): 8.82 (1H, d, J = 2.2, H-5), 8.37 (1H, dd, J = 2.5, 9.0, H-7), 7.59 (1H, d, J = 9.0, H-8), 7.59 (1H, br.s, H-12), 7.48 (1H, s, H-4′), 6.82 (1H, d, J = 3.7, H-2′), 6.36 (1H, dd, J = 1.8, 3.7, H-3′), 4.21 (2H, t, J = 7.2, H-11), 3.23 (2H, t, J = 6.8, H-10).

Mass spectrum (*m*/*z*, %): 309 (86) $[M]^+$, 229 (1.4) $[M - (CH - Ar)]^+$, 308 (100), 280 (58.7), 268 (61.5), 262 (33.6), 250 (29), 234 (54.5), 222 (37.8), 208 (39), 205 (57), 192 (8), 179 (15.4), 152 (9.4), 143 (7).

Perchlorate of 3i (4i): $C_{16}H_{12}O_8N_3Cl$, yield 70%, mp 202°C (dec.).

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