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DIRECTIONS OF REACTIONS OF 6-AMINO-, -ACETYLAMINO-, AND -BENZOYLAMINODEOXYVASICINONES WITH ALDEHYDES

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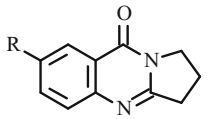
*6-Acetylamino- and -benzoylamino-9-arylidenedeoxyvasicinones were synthesized by reaction of 6-amino- (**3**), -acetylamino- (**4**), and -benzoylamino- (**5**) -deoxyvasicinones (DOV) with aromatic aldehydes and furfurol in glacial acetic acid. It was shown that the amino group of 6-aminodeoxyvasicinone underwent acylation upon reaction with aldehydes to form 6-acetylamino-DOV, which reacted with aldehydes to form 9-arylidene derivatives. Carrying out this condensation in toluene, o-xylene, and ethanol produced a mixture of condensation products at the 6-amino- and α-CH_2-groups. It was found that condensati on of **3** with 4-nitrobenzaldehyde in pyridine formed exclusively the Schiff bases. Methods for preparing 6-nitrodeoxyvasicinone and for its reduction were improved.*

Keywords: deoxyvasicinone, aldehydes, condensation.

We studied previously condensation of 6-bromo(nitro)-6,8-dibromo derivatives of the alkaloid deoxyvasicinone (**1**) with aliphatic, aromatic, and heterocyclic unsaturated aldehydes by fusion of equimolar amounts of reagents [1, 2] and in refluxing glacial acetic acid [3]. It was found that the reaction occurred only with aromatic and heterocyclic aldehydes [4–6]. Aliphatic and unsaturated aldehydes did not react. It was also shown that the direction of the reaction depended on the nature of the substituent in the aldehyde aromatic ring and the conditions [7–10].

In order to expand the condensation of deoxyvasicinones (DOV) with aldehydes to other 6-substituted DOV, we studied the reaction of 6-amino-, -acetylamino-, and -benzoylamino-DOV with aromatic (benzaldehyde, 4-hydroxy-, -dimethylamino-, -nitro-, and 3,4-dimethoxybenzaldehydes) aldehydes and furfurol [11]:



1 - 5

R = H (**1**); NO_2 (**2**); NH_2 (**3**); $NHCOCH_3$ (**4**); $NHCOC_6H_5$ (**5**)

6-Nitrodeoxyvasicinone (**2**) was prepared by nitration of deoxyvasicinone (**1**) by an improved method in high yield (88%) compared with the known method [12]. Reduction of **2** by $SnCl_2 \cdot 2H_2O$ in a 3:1 ratio synthesized 6-aminodeoxyvasicinone (**3**) in almost quantitative (96%) yield.

The presence of two potential reaction centers, the amino and α-methylene groups, in 6-aminodeoxyvasicinone (**3**) suggested that the reaction with aldehydes could occur at one or simultaneously at both centers. Thus, formation of mono- or bisarylidene derivatives in addition to Schiff bases could be expected. We studied the reaction of **3** with aromatic aldehydes (**6a-e**) in toluene, *o*-xylene, EtOH, and Py under various conditions. The reaction of **3** with the aforementioned aldehydes in toluene and *o*-xylene did not give the desired results because of the formation of a complicated product mixture, from which pure compounds could not be isolated. Performing the reaction of 4-nitrobenzaldehyde (**6d**) and **3** in Py at +5–6°C showed that the condensation proceeded slowly. A crystalline precipitate began to form only after a week. The mixture was held at this temperature for five weeks in order to complete the reaction. The yield of 6-*N*-(4′-nitrobenzylidene)aminodeoxyvasicinone (**7**) was 48%.

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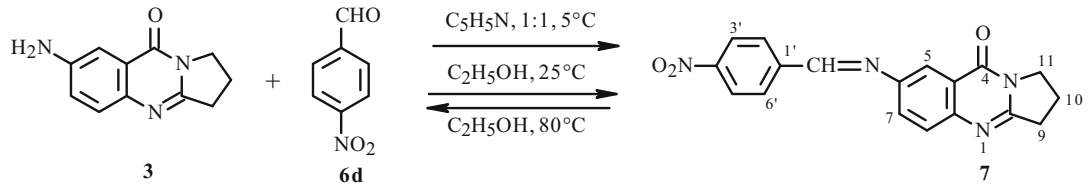


3 **6d** **7**

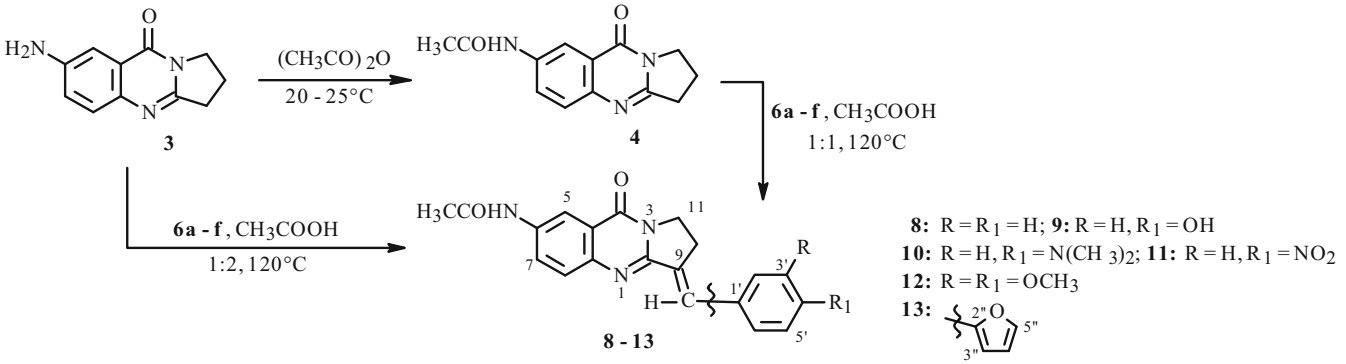
The reaction in a protic solvent, alcohol, went faster. However, the resulting Schiff base (**7**) was difficult to isolate pure because of the presence in the mixture of unreacted starting amine (**3**). Furthermore, the resulting azomethine decomposed easily during the purification to starting **3** and the corresponding aromatic aldehyde.

The reaction with aromatic aldehydes with electron-donating substituents [OH, $N(CH_3)_2$, OCH_3] in the benzene ring went even more difficultly. Pure products could not be isolated, like for the reaction in protic solvents.

The resulting Schiff base also decomposed to 6-aminodeoxyvasicinone upon recrystallization from alcohol. We verified this fact by studying the ability to decompose **7** by refluxing in EtOH for 1.5 h, observing during this its complete decomposition and formation of **3** and **6d**. Storing the reaction mixture after hydrolysis at room temperature caused the precipitate of **3** to react with **6d** and **7** to reprecipitate in 35% yield (TLC monitoring). However, the condensation went very slowly. All this means that the formation of the azomethines was reversible.

We showed earlier that the reaction of **1** with aldehydes is accelerated in acidic medium [1]. The rate of the reaction of **3** with aldehydes (**6a**–**f**) was increased by performing it with a **3**:aldehyde ratio of 1:2 in glacial acetic acid. It was expected that both mono- and bisarylidene derivatives would form. However, condensation of **3** with aldehydes in refluxing glacial acetic acid for 1–3 h instead of the expected gave 6-acetylamino-9-arylidenedeoxyvasicinones (**8**–**13**), i.e., simultaneous acetylation of the amino group of **3** and condensation with aldehydes exclusively at the α-methylene group were observed. Formation of 6-acetylaminodeoxyvasicinone (**4**) from **3** was observed earlier during reduction of 6-nitrodeoxyvasicinone (**2**) by a defatted gland in glacial acetic acid [13].

Alternate syntheses of **8**–**13** were performed in order to confirm that the reaction could proceed through initial acylation and to prove the structures of the products. Starting 6-acetylaminodeoxyvasicinone (**4**) that was required for this was prepared by acetylation of **3** with acetic anhydride at room temperature. Compound **4** was condensed with aldehydes (**6a**–**f**) by refluxing in glacial acetic acid equimolar amounts of the reagents for 3–5 h to produce 6-acetylamino-9-arylidenedeoxyvasicinones (**8**–**13**) in good yields.



3 **4** **8 - 13**

The physicochemical properties of **8**–**13** prepared by the two methods were identical.

6-Benzoylaminodeoxyvasicinone (**5**) was synthesized in high yield (95%) by reaction of **3** with benzoyl chloride in the presence of triethylamine in anhydrous benzene. Condensation of **5** with aldehydes (**6a**–**f**) was carried out analogous to the reaction of **4** to afford the corresponding 6-benzoylamino-9-arylidenedeoxyvasicinones (**14**–**19**).

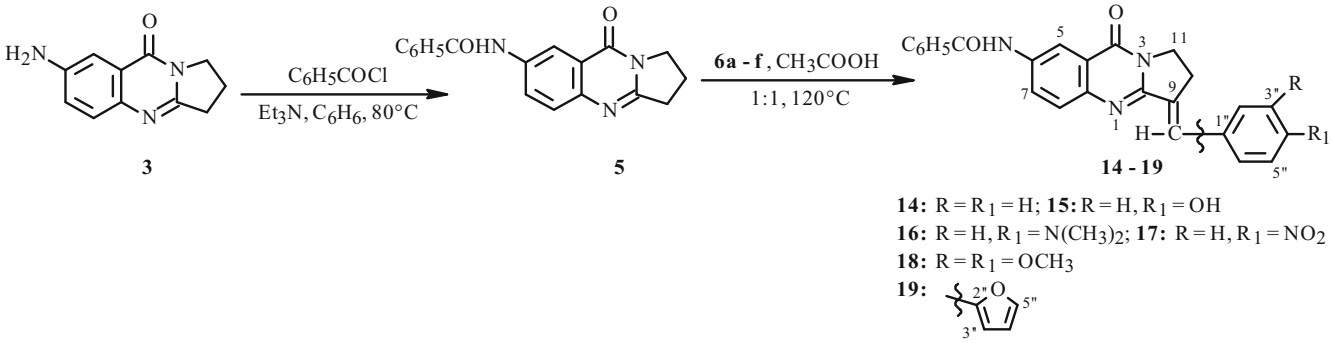
These results led to the conclusion that **3** can react differently with carbonyl compounds depending on the conditions. Condensation in Py forms Schiff bases (example of **6d**) whereas performing the reaction in acetic acid favors acetylation of the amino group and further reaction with aromatic aldehydes.

The structures of synthesized **3**, **5**, **7**–**19** were confirmed by mass spectrometry and PMR spectroscopy.

The PMR spectrum of **7** showed methylene protons in the α-position at 3.05 ppm (2H, triplet), protons in the β-position with CS at 2.13 ppm (2H, multiplet), and in the γ-position, 4.03 ppm (2H, triplet). The mass spectrum contained a strong peak for the molecular ion $[M]^+$ (334). These results led to the conclusion that the reaction of **3** and 4-nitrobenzaldehyde occurred only at the amino group.

Protons of methylenes in the β-position in **8-19** had CS in the range 3.12–3.22 ppm (2H, triplet); in the γ-position, at 4.18–4.28 ppm (2H, triplet). Methyl protons of the $N(CH_3)_2$ group in **10** and **16** appeared at 3.07–3.08 ppm (6H, singlet); of the OCH_3 groups in **12** and **18**, at 3.60–3.61 ppm (3H, singlet). Aromatic protons were observed at 6.32–8.48 ppm. Methyl protons of the acetyl in **8–13** appeared as singlets (3H) in the range 2.01–2.03 ppm.

The appearance of protons of the β- and γ-methylenes as two triplets and the lack of protons of the α-carbon atom at 2.9–3.0 ppm confirmed unambiguously that the condensation occurrred exclusively at the α-carbon atom.



EXPERIMENTAL

Mass spectra were taken in an MS-30 instrument (Kratos); PMR spectra, in TFA + CD_3COOD, TFA + $(CD_3)_2SO$, and Py-d_5 on a Unity 400+ instrument (operating frequency 400 MHz, HMDS internal standard, δ scale). Melting points of the synthesized compounds were determined on Boetius (Germany) and Mel-Temp (USA) apparatuses. The purity of products and course of reactions were monitored by TLC on Sorbfil (Russia) and Whatman UV-254 (Germany) plates using benzene:MeOH (2:1, system A; 3:1, system B; 5:1, system C).

6-Nitrodeoxyvasicinone (2) was synthesized by a modified method [8]. Deoxyvasicinone (**1**, 20 g, 0.107 mol) was dissolved in conc. H_2SO_4 (40 mL, 95.72%, ρ = 1.835 g/cm^3) with vigorous stirring and cooling (ice bath), treated dropwise at <2°C with a nitrating mixture consisting of nitric (15 mL, 59.69%, ρ = 1.365 g/cm^3) and sulfuric (15 mL, ρ = 1.835 g/cm^3) acids, stirred at 5–10°C for 1 h and for the same time at room temperature, and poured onto ice. The resulting yellow precipitate was filtered off, washed with water until neutral, and dried to afford **2** (21.8 g, 88%), mp 188–189°C (MeOH), in agreement with the literature [8].

6-Aminodeoxyvasicinone (3) was synthesized by the method for reducing *m*-nitrobenzaldehyde to *m*-aminobenzaldehyde [14]. Tin chloride ($SnCl_2 \cdot 2H_2O$, 23 g, 102 mmol) was placed into a three-necked flask equipped with a mechanical stirrer and dropping funnel, cooled (ice bath), stirred, treated with conc. HCl (31 mL, 36%), stirred for 10–15 min, treated in portions with a suspension consisting of **2** (8 g, 34 mmol), EtOH (48 mL), and conc. HCl (16 mL), and stirred for another 10–15 min with cooling. The ice bath was removed. Stirring was continued at room temperature (0.5 h). The reaction was continued with vigorous stirring on a boiling water bath for 2 h. The mixture was left overnight, diluted with water, and neutralized with NaOH solution (10%) until the pH was 11. The resulting precipitate was filtered off, washed with distilled water until neutral, and dried. Recrystallization from EtOH produced **3** (6.67 g, 96%), mp 253–254°C, R_f 0.61 (system B) (lit. [12] mp 248–249°C).

PMR spectrum (δ, ppm, J/Hz): 8.25 (1H, d, J = 2.6, H-5), 7.79 (1H, dd, J = 2.6, 8.8, H-7), 7.57 (1H, d, J = 8.8, H-8), 4.14 (2H, t, J = 7.2, H-11), 3.34 (2H, t, J = 7.8, H-9), 2.18-2.24 (2H, m, H-10).

6-Acetylaminodeoxyvasicinone (4). Compound **3** (3 g, 15 mmol) was treated with acetic anhydride (20 mL). A white precipitate began to form immediately. The mixture was left overnight. The precipitate was filtered off, washed with benzene, and dried. Recrystallization from EtOH afforded **4** (3.4 g, 94%), mp 265–266°C, in agreement with the literature [12].

6-Benzoylaminodeoxyvasicinone (5). A mixture of **3** (3 g, 15 mmol), benzoyl chloride (2.24 mL, 2.73 g, 19.5 mmol, ρ = 1.2187 g/cm^3), and freshly distilled Et_3N (2.72 mL, 19.5 mmol, ρ = 0.7229 g/cm^3) in anhydrous benzene

(200 mL) was refluxed on a water bath for 4 h and cooled to room temperature. The resulting crystals were filtered off, washed first with benzene and then with water, and dried. Recrystallization from EtOH afforded **5** (4.34 g, 95%), mp 258–260°C (EtOH), R_f 0.25 (system B).

PMR spectrum (δ, ppm, J/Hz): 9.09 (1H, d, J = 2.5, H-5), 8.59 (1H, s, NH), 8.42 (1H, dd, J = 2.5, 8.6, H-7), 8.13–8.15 (2H, m, H-2′,6′), 7.74 (1H, d, J = 8.6, H-8), 7.26-7.33 (3H, m, H-3′,4′,5′), 3.86 (2H, t, J = 7.1, H-11), 2.80 (2H, t, J = 7.8, H-9), 1.72-1.74 (2H, m, H-10).

6-*N*-(4′-Nitrobenzylidene)aminodeoxyvasicinone (7). Method A. Compound **3** (0.1 g, 0.5 mmol) and 4-nitrobenzaldehyde (**6d**, 79 mg, 0.52 mmol) were dissolved in freshly distilled Py (5 mL) and left at +5–6°C for five weeks. The course of the reaction was monitored by TLC. The resulting crystals were filtered off, washed several times with cyclohexane, and dried to afford **7** (80 mg, 48%), mp 258–260°C, R_f 0.74 (system B).

PMR spectrum (δ, ppm, J/Hz): 8.93 (1H, s, H-12), 8.33 (2H, d, J = 8.7, H-3′,5′), 8.19 (2H, d, J = 8.7, H-2′,6′), 7.98 (1H, d, J = 2.5, H-5), 7.78 (1H, dd, J = 2.5, 8.7, H-7), 7.63 (1H, d, J = 8.7, H-8), 4.03 (2H, t, J = 7.2, H-11), 3.05 (2H, t, J = 8.1, H-9), 2.13 (2H, m, H-10).

Mass spectrum (*m*/*z*, *I*rel, %): 334 (93) $[M]^+$, 304 (100) $[M - NO]^+$, 303 (66.2), 288 (12.4) $[M - NO_2]^+$, 287 (29), 212 (2.0) $[M - C_6H_4 - NO_2]^+$, 185 (11) $[M - N{=}CH{-}C_6H_4{-}NO_2]^+$, 157 (4.8), 143 (2), 131 (5.5), 118 (18.6), 101 (14.5).

Method B. A mixture of **3** (0.3 g, 1.5 mmol) and 4-nitrobenzaldehyde (**6d**, 0.24 g, 1.6 mmol) in EtOH (20 mL) was stirred at room temperature for 2 h. The resulting precipitate was filtered off, washed with EtOH, and dried to afford a mixture of compounds (0.48 g) in overall yield (96.4%) that consisted of unreacted **3** (20%), R_f 0.61 (system B), and **7** (80%), R_f 0.74 (system B).

6-Acetylamino-9-benzylidenedeoxyvasicinone (8). Method A. Compound **4** (0.3 g, 1.2 mmol) was dissolved in glacial acetic acid (3 mL), treated with benzaldehyde (0.13 mL, 0.138 g, 1.3 mmol, ρ = 1.0498 g/cm^3), refluxed for 3-5 h, and left overnight. Solvent was distilled off. The solid was recrystallized from aqueous DMF to afford **8** (0.209 g, 52.2%), mp 348–350°C, R_f 0.75 (system A).

Method B. Compound **3** (0.201 g, 1 mmol) and benzaldehyde (0.2 mL, 0.21 g, 2.0 mmol, ρ = 1.0498 g/cm^3) were dissolved in glacial acetic acid (5 mL), refluxed for 1–3 h, and left overnight. The resulting crystals were filtered off, washed with water, and dried. Recrystallization from aqueous DMF afforded **8** (0.229 g, 70%).

A mixed melting sample of **8** prepared by methods A and B did not give depression.

PMR spectrum (δ, ppm, J/Hz): 8.85 (1H, s, NH), 8.28 (1H, d, J = 2.2, H-5), 7.84 (1H, dd, J = 2.2, 9.1, H-7), 7.69 (1H, d, J = 2.6, H-12), 7.47 (1H, d, J = 9.1, H-8), 7.23 (2H, dd, J = 1.8, 8.0, H-2′,6′), 7.14-7.17 (3H, m, H-3′,4′,5′), 4.22 (2H, t, J = 6.9, H-11), 3.17 (2H, td, J = 6.9, 2.6, H-10), 2.01 (3H, s, CH_3CO).

6-Acetylamino-9-(4′-hydroxybenzylidene)deoxyvasicinone (9). Method A. Analogously to that described above, **4** (0.3 g, 1.2 mmol) and 4-hydroxybenzaldehyde (0.159 g, 1.3 mmol) afforded **9** (0.297 g, 69.4%), mp 378–380°C (aq. DMF), R_f 0.57 (system B).

Method B. Compound **3** (0.1 g, 0.5 mmol) and 4-hydroxybenzaldehyde (0.122 g, 1 mmol) according to the above method afforded **9** (0.167 g, 87%).

PMR spectrum (δ, ppm, J/Hz): 8.84 (1H, s, NH), 8.24 (1H, d, J = 2.2, H-5), 7.83 (1H, dd, J = 2.2, 9.1, H-7), 7.62 (1H, br.s, H-12), 7.43 (1H, d, J = 9.1, H-8), 7.21 (2H, d, J = 8.7, H-2′,6′), 6.70 (2H, d, J = 8.7, H-3′,5′), 4.21 (2H, t, J = 7.3, H-11), 3.12 (2H, t, J = 7.3, H-10), 2.01 (3H, s, CH_3CO).

6-Acetylamino-9-(4′-dimethylaminobenzylidene)deoxyvasicinone (10). Method A. Compound **4** (0.2 g, 0.8 mmol) and 4-dimethylaminobenzaldehyde (0.129 g, 0.86 mmol) analogously to that described above afforded **10** (0.249 g, 81%), mp 380°C (dec.) (DMF), R_f 0.74 (system A).

Method B. Analogously to that described above **3** (0.201 g, 1 mmol) and 4-dimethylaminobenzaldehyde (0.298 g, 2 mmol) afforded **10** (0.304 g, 82%).

PMR spectrum (δ, ppm, J/Hz): 9.04 (1H, s, NH), 8.38 (1H, d, J = 2.3, H-5), 7.80 (1H, dd, J = 2.3, 8.9, H-7), 7.77 (1H, s, H-12), 7.55 (1H, d, J = 8.9, H-8), 7.50 (2H, d, J = 8.9, H-2′,6′), 7.43 (2H, d, J = 8.9, H-3′,5′), 4.25 (2H, t, H-11), 3.18 (2H, t, H-10), 3.08 [6H, s, $N(CH_3)_2$], 2.03 (3H, s, CH_3CO).

Mass spectrum (*m*/*z*, I_{rel}, %): 374 (100) $[M]^+$, 359 (6) $[M - CH_3]^+$, 331 (29.8) $[M - COCH_3]^+$, 315 (8.3) $[M - NCOCH_3]^+$, 241 (2.0) $[M - CHC_6H_4N(CH_3)_2]^+$, 186 (1.6), 166 (10.4), 134 (8.3), 101 (3.5).

6-Acetylamino-9-(4′-nitrobenzylidene)deoxyvasicinone (11). Method A. The reaction was carried out analogously to that described above using **4** (0.2 g, 0.8 mmol) and 4-nitrobenzaldehyde (0.13 g, 0.86 mmol) to afford **11** (0.183 g, 60%), mp 346–348°C (DMF), R_f 0.73 (system A).

Method B. Analogously to that described above **3** (0.201 g, 1 mmol) and 4-nitrobenzaldehyde (0.302 g, 2 mmol) afforded **11** (0.336 g, 90%).

PMR spectrum (δ, ppm, J/Hz): 8.98 (1H, s, NH), 8.36 (1H, s, H-5), 8.00 (1H, d, J = 8.1, H-3′,5′), 7.81 (1H, d, J = 8.9, H-7), 7.78 (1H, s, H-12), 7.54 (1H, d, J = 8.9, H-8), 7.44 (2H, d, J = 8.1, H-2′,6′), 4.26 (2H, t, H-11), 3.21 (2H, t, H-10), 2.02 (3H, s, CH_3CO).

Mass spectrum (*m*/*z*, I_{rel}, %): 376 (100) $[M]^+$, 346 (52.8), 345 (50.7), 333 (50) $[M - COCH_3]^+$, 303 (52), 318 (4.8) $[M - NHCOCH_3]^+$, 287 (50), 231 (17.4), 198 (18), 184 (3.5), 143 (9.0), 130 (8.3), 101 (6.2).

6-Acetylamino-9-(3′,4′-dimethoxybenzylidene)deoxyvasicinone (12). Method A. Analogously to that described above **4** (0.3 g, 1.2 mmol) and 3,4-dimethoxybenzaldehyde (0.216 g, 1.3 mmol) afforded **12** (0.26 g, 54%), $C_{22}H_{21}O_4N_3$, mp 314–316°C (aq. DMF), R_f 0.70 (system B).

Method B. Compound **3** (0.1 g, 0.5 mmol) and 3,4-dimethoxybenzaldehyde (0.166 g, 1 mmol) according to the above method afforded **12** (0.190 g, 88%).

PMR spectrum (δ, ppm, J/Hz): 9.01 (1H, s, NH), 8.31 (1H, s, H-5), 7.75 (1H, d, J = 8.9, H-7), 7.66 (1H, s, H-12), 7.47 (1H, d, J = 7.7, H-6′), 7.02 (1H, d, J = 8.9, H-8), 6.85 (1H, s, H-2′), 6.77 (1H, d, J = 7.7, H-5′), 4.22 (2H, t, H-11), 3.59 [6H, s, $(OCH_3)_2$], 3.17 (2H, t, H-10), 2.02 (3H, s, CH_3CO).

6-Acetylamino-9-(furfurylidene-2′)deoxyvasicinone (13). Method A. Analogously to that described above **4** (0.3 g, 1.2 mmol) and furfurol (0.11 mL, 0.127 g, 1.3 mmol, ρ = 1.1598 g/cm^3) afforded **13** (0.323 g, 81.6%), $C_{18}H_{15}O_3N_3$, mp 316–318°C (aq. DMF), R_f 0.77 (system B).

Method B. Compound **3** (0.1 g, 0.5 mmol) and furfurol (0.082 mL, 0.096 g, 1.0 mmol, ρ = 1.1598 g/cm^3) afforded **13** (0.14 g, 87%), $C_{18}H_{15}O_3N_3$, mp 316–318°C (aq. DMF), R_f 0.77 (system B).

PMR spectrum (δ, ppm, J/Hz): 8.84 (1H, s, NH), 8.23 (1H, d, J = 2.2, H-5), 7.82 (1H, dd, J = 2.2, 8.7, H-7), 7.42–7.47 (3H, m, H-8,12,5′), 6.72 (1H, d, J = 3.6, H-3′), 6.31 (1H, dd, J = 1.8, 3.6, H-4′), 4.18 (2H, t, J 7.3, H-11), 3.20 (2H, t, J = 7.3, H-10), 2.01 (3H, s, CH_3CO).

6-Benzoylamino-9-benzylidenedeoxyvasicinone (14). Compound **5** (0.305 g, 1.0 mmol) was dissolved in glacial acetic acid (5 mL), treated with benzaldehyde (0.12 mL, 0.126 g, 1.19 mmol, ρ = 1.0498 g/cm^3) and refluxed for 3–5 h. Solvent was distilled off. The solid was recrystallized from aqueous DMF to afford **14** (2.55 g, 64.8%), mp 288–290°C, R_f 0.58 (system B).

PMR spectrum (δ, ppm, J/Hz): 9.03 (1H, s, NH), 8.42 (1H, d, J = 2.5, H-5), 7.99 (1H, dd, J = 2.5, 9.1, H-7), 7.71 (1H, t, J = 2.8, H-12), 7.53 (1H, d, J = 9.1, H-8), 7.48 (2H, t, J = 7.4, 8.8, H-3′,5′), 7.24–7.26 (3H, m, H-3′,4′,5′), 7.14–7.17 (5H, m, H-2′,6′,2″,4″,6″), 4.22 (2H, t, J = 7.0, H-11), 3.19 (2H, t, J = 7.0, 2.8, H-10).

6-Benzoylamino-9-(4″-hydroxybenzylidene)deoxyvasicinone (15). Analogously to that described above **5** (0.15 g, 0.5 mmol) and 4-hydroxybenzaldehyde (0.073 g, 0.6 mmol) afforded **15** (0.124 g, 62%), mp 339–341°C (aq. DMF), R_f 0.64 (system B).

PMR spectrum (δ, ppm, J/Hz): 9.01 (1H, s, NH), 8.39 (1H, d, J = 2.1, H-5), 7.98 (1H, d, J = 8.8, H-7), 7.64 (1H, s, H-12), 7.49 (3H, d, J = 8.8, H-8, 2″,6″), 7.22–7.25 (3H, m, H-2′,4′,6′), 7.14 (2H, t, J = 7.7, H-3′,5′), 6.71 (2H, d, J = 8.8, H-3″,5″), 4.23 (2H, t, J = 7.0, H-11), 3.13 (2H, t, J = 7.0, H-10).

6-Benzoylamino-9-(4″-dimethylaminobenzylidene)deoxyvasicinone (16). Compound **5** (0.305 g, 1.0 mmol) and 4-dimethylaminobanzaldehyde (0.164 g, 1.61 mmol) analogously to that described above afforded **16** (0.337 g, 86.5%), mp 320–322°C (aq. DMF), R_f 0.68 (system B).

PMR spectrum (δ, ppm, J/Hz): 9.03 (1H, s, NH), 8.48 (1H, d, J = 2.3, H-5), 8.00 (1H, dd, J = 2.3, 8.9, H-7), 7.76 (1H, t, J = 5.5, H-12), 7.58 (1H, d, J = 8.9, H-8), 7.49 (4H, dd, J = 8.2, H-2″,3″,5″,6″), 7.41 (2H, dd, J = 8.9, H-2′,6′), 7.27 (1H, tt, J = 8.8, H-4′), 7.14 (1H, t, J = 8.8, H-3′,5′), 4.27 (2H, t, J = 6.8, H-11), 3.18 (2H, t, J = 6.8, 5.5, H-10), 3.07 [6H, s, $N(CH_3)_2$].

6-Benzoylamino-9-(4″-nitrobenzylidene)deoxyvasicinone (17). The reaction was carried out analogously to that described above. Compound **5** (0.305 g, 1.0 mmol) and 4-nitrobenzaldehyde (0.166 g, 1.1 mmol) afforded **17** (0.27 g, 61.6%), mp 326–327°C (aq. DMF), R_f 0.74 (system B).

PMR spectrum (δ, ppm, J/Hz): 9.07 (1H, s, NH), 8.48 (1H, d, J = 2.5, H-5), 8.02 (3H, d, J = 8.8, H-7, 3″,5″), 7.81 (1H, d, J = 2.8, H-12), 7.60 (1H, d, J = 8.8, H-8), 7.50 (2H, d, J = 7.4, H-2′,6′), 7.45 (2H, d, J = 8.8, H-2″,6″), 7.27 (1H, t, J = 7.4, H-4′), 7.14 (2H, t, J = 7.4, H-3′,5′), 4.28 (2H, t, J = 7.0, H-11), 3.22 (2H, t, J = 7.0, 2.8, H-10).

6-Benzoylamino-9-(3″,4″-dimethoxybenzylidene)deoxyvasicinone (18). Analogously to that described above **5** (0.305 g, 1.0 mmol) and 3,4-dimethoxybenzaldehyde (0.18 g, 1.1 mmol) afforded **18** (0.384 g, 84.7%), mp 314–316°C (aq. DMF), R_f 0.57 (system B).

PMR spectrum (δ, ppm, J/Hz): 9.03 (1H, s, NH), 8.40 (1H, d, J = 2.4, H-5), 7.98 (1H, dd, J = 2.4, 8.9, H-7), 7.67 (1H, t, J = 2.4, H-12), 7.53 (1H, d, J = 8.9, H-8), 7.50 (2H, d, J = 7.5, H-2′,6′), 7.26 (1H, tt, J = 1.4, 7.5, H-4′), 7.14 (2H, t, J = 7.5, H-3′,5′), 7.02 (1H, dd, J = 2.0, 8.9, H-6″), 6.85 (1H, d, J = 2.0, H-2″), 6.76 (1H, d, J = 8.9, H-5″), 4.24 (2H, t, J = 7.1, H-11), 3.61 (3H, s, OC$\underline{H}_3$-3″), 3.60 (3H, s, OC$\underline{H}_3$-4″), 3.18 (2H, t, J = 7.1, 2.4, H-10).

6-Benzoylamino-9-(furfurylidene-2″)deoxyvasicinone (19). Compound **5** (0.305 g, 1.0 mmol) and furfurol (0.1 mL, 0.116 g, 1.2 mmol, ρ = 1.1598 g/cm^3) analogously to that described above afforded **19** (0.196 g, 51.2%), mp 296–298°C (aq. DMF), *Rf* 0.76 (system B).

PMR spectrum (δ, ppm, J/Hz): 9.02 (1H, s, NH), 8.38 (1H, d, J = 2.5, H-5), 7.97 (2H, dd, J = 2.5, 9.1, H-7), 7.49–7.50 (4H, m, H-8, 12, 2′,6′), 7.44 (1H, d, J = 1.7, H-5″), 7.26 (1H, t, J = 7.4, H-4′), 7.14 (2H, t, J = 7.4, H-3′,5′), 6.73 (1H, t, J = 3.8, H-3″), 6.32 (1H, dd, J = 1.7, 3.8, H-4″), 4.20 (2H, t, J = 7.0, H-11), 3.21 (2H, t, J = 7.0, H-10).

Decomposition of 6-*N*-(4′-nitrobenzylidene)aminodeoxyvasicinone (7) in Alcohol. A round-bottomed flask was charged with **7** (12 mg, 0.036 mmol) and EtOH (10 mL). The mixture was refluxed for 1.5 h. After **7** disappeared completely (TLC monitoring), the mixture was cooled to room temperature. The resulting precipitate was filtered off, washed with EtOH, and dried to afford **3** (6.86 mg, 98%), mp 253–254°C (EtOH), R_f 0.61 (system B). Solvent was removed from the mother liquor to afford **6d** (5 mg, 92%), mp 105–106°C (H_2O), R_f 0.80 (system B).

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