

Synthesis of 4-(4-dimethylaminophenyl)-2-methyl-1-pyrroline

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Addition of nitromethane to 4-(4-*N,N*-dimethylaminophenyl)-3-buten-2-one (*II*) afforded 4-(4-*N,N*-dimethylaminophenyl)-5-nitro-2-pentanone; carbonyl group of the latter was protected, the nitro group was reduced with lithium hydridoaluminate and the resulting amine was cyclized to the required 4-(4-*N,N*-dimethylaminophenyl)-2-methyl-1-pyrroline. Addition of further *C*-acids to the double bond of compound *II* is also described; derivatives of cinnamic acid isolated in this process originated by a retrogressive Michael addition.

В результате присоединения нитрометана к 4-(4-*N,N*-диметиламинофенил)-3-бутен-2-ону (*II*) был получен 4-(4-*N,N*-диметиламинофенил)-5-нитро-2-пентанон; карбонильная группа последнего была защищена, нитро-группа восстановлена алюмогидридом лития, и образовавшийся амин циклизировался с образованием желаемого 4-(4-*N,N*-диметиламинофенил)-2-метил-1-пирролина. Описывается также присоединение *C*-кислот по двойной связи соединения *II*; производные коричневой кислоты, выделенные в этом процессе, образовались в результате обратного присоединения по Михаэлл.

The steroidal alkaloid veracintine, isolated from the above-ground part of *Veratrum album* ssp. *Lobelianum* [1] was found to be biologically active; its antileukemic effect is subject to the presence of pyrroline ring [2]. Preparation of some simple models having the pyrroline ring was stimulated by the need to study the biological properties in more detail. This paper concerns the synthesis of 4-(4-*N,N*-dimethylaminophenyl)-2-methyl-1-pyrroline (*I*). Synthone for the synthesis, 4-(4-*N,N*-dimethylaminophenyl)-3-buten-2-one (*II*) displayed in its UV spectrum absorption bands at $\lambda = 340$ nm and 251 nm and at $\tilde{\nu} = 1660$ cm^{-1} in the IR spectrum, both indicative of an α,β -unsaturated ketone. The nitro derivative *III* resulting from nitration of *II* with nitromethane showed in the UV spectrum only one band at $\lambda = 258$ nm due to a disrupted conjugation, whilst the band of the carbonyl group in the IR spectrum was shifted to $\tilde{\nu} = 1715$ cm^{-1} . The carbonyl group of *III* was protected with ethylene glycol under formation of the 1,3-dioxolane derivative *IV*. Instead of the carbonyl group absorption bands at $\tilde{\nu} = 1200$ cm^{-1} ($\nu_s(\text{C—O—C})$) and $\tilde{\nu} = 820$ cm^{-1}

($\nu_{\text{as}}(\text{C—O—C})$) characterizing the dioxolane grouping appeared in its IR spectrum; its four equivalent protons were seen in the $^1\text{H NMR}$ spectrum as a singlet at $\delta = 3.90$ ppm. Mass spectrum of *IV* had a prominent peak at $m/z = 87$ ($\text{C}_4\text{H}_7\text{O}_2$). It is generally known that nitro groups linked to an aliphatic residue are more stable against hydrogenation than those bound to an aromatic system. Methods suitable for reduction are *e.g.* the catalytic reductions over palladium [3], Adams catalyst [4] and Raney nickel [5], reduction with complex hydrides [6], hydrazine [7], *etc.* The nitro group of *IV* was reduced with lithium tetrahydridoaluminate in tetrahydrofuran. The resulting aminoketal *V* was characterized as the acetamide *VI*. The carbonyl group of *V* was freed by decomposition of the dioxolane ring with dilute hydrochloric acid and intramolecularly cyclized with the primary amino group to the 4-substituted 2-methyl-1-pyrroline *I*. This compound reveals in the UV spectrum a band associated with the benzene ring at $\lambda = 257$ nm, and another one in the IR spectrum at $\tilde{\nu} = 1650$ cm^{-1} due to vibration of the $\text{C} = \text{N}$ grouping. The peak of the radical ion is the parent peak of *I*. Since the methyl group in *I* is bound to an sp^2 carbon, the signal of its protons was downfield shifted in the $^1\text{H NMR}$ spectrum to $\delta = 2.08$ ppm. Signals of H-3a, H-3b, H-4, H-5a, H-5b protons form a five-spin system in which also four-valent interactions among H-3a, H-3b and H-5a, H-5b were manifested in addition to two- and three-valent ones, this being indicative of closure of the pyrroline ring. Due to great flexibility of the five-membered pyrroline ring these values represent the mean values of coupling constants and therefore, the exact conformation could not be ascribed at this stage.

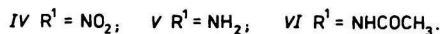
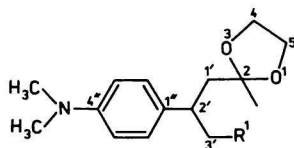
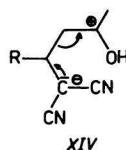
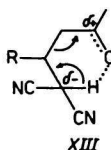
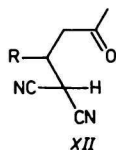
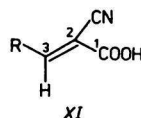
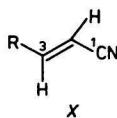
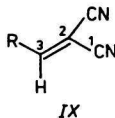
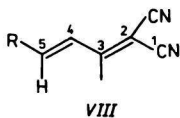
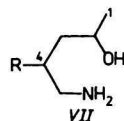
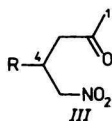
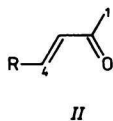
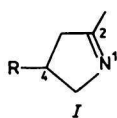
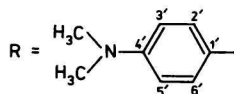
Some amino alcohols were reported to have an antiarrhythmic effect [8], and therefore amino alcohol *VII* was prepared by reduction of the nitroketone *III* with lithium tetrahydridoaluminate. The chalcone *II* was also the starting material for additions of further *C*-acids to its double bond. Thus, malonodinitrile in benzene furnished compounds *VIII* and *IX* in the presence of triethylamine and the sole compound *IX* when using pyridine. Compounds *VIII* ($\text{C}_{15}\text{H}_{15}\text{N}_3$) and *IX* ($\text{C}_{12}\text{H}_{11}\text{N}_3$) displayed in their IR spectra absorption bands at $\tilde{\nu} = 2200$ cm^{-1} ($\nu(\text{C} \equiv \text{N})$) and molecular radical ion peaks (100% relative intensity) in their mass spectra. The analysis of ^1H and $^{13}\text{C NMR}$ spectral data made it possible to assign the structure of (*4E,3-s-trans*)-5-(4'-*N,N*-dimethylaminophenyl)-2-cyano-3-methyl-2,4-pentadienic acid nitrile to compound *VIII*, and of 4'-*N,N*-dimethylamino-2-cyanocinnamic acid nitrile to *IX*. Protons H-4 and H-5 of compound *VIII* resonate at $\delta = 7.19$ ppm and 7.25 ppm as an AB quartet with coupling constant $J_{4,5} = 15.5$ Hz, this being in favour of their *trans* arrangement. Signals of H-5 are broadened due to a four-valent interaction with the benzene ring protons, as followed from the two-dimensional correlation experiment optimized to long-range coupling constants [9]. The spatial interaction between protons of the methylene group attached to C-3 and H'-5 protons,

but not with H-4 protons could be observed in the two-dimensional NOE spectrum; this observation backed the 3-*s*-configuration for *VIII*. The signal of the quaternary carbon C-2 in the ^{13}C NMR spectrum was shifted towards an extraordinarily low value ($\delta = 71.6$ ppm) due to cumulative shielding effect of two nitrile groups and the benzene ring. Signals of the nitrile groups at $\delta = 116.0$ ppm and 114.9 ppm in *cis* and *trans* position in respect to H-3, respectively, were distinguished according to the magnitude of the three-valent coupling constant $^1\text{H}-^{13}\text{C}$ ($J(\text{H-3}, \text{CN}_{\text{cis}}) = 8.1$ Hz, $J(\text{H-3}, \text{CN}_{\text{trans}}) = 13.7$ Hz). Two compounds were isolated after addition of methyl cyanoacetate to the chalcone *II* double bond in methanol in the presence of sodium methoxide: (*2E*)-4'-*N,N*-dimethylaminocinnamic acid nitrile (*X*) and (*2E*)-4'-*N,N*-dimethylamino-2-cyanocinnamic acid (*XI*). Coupling constant $J_{2,3} = 16.4$ Hz for compound *X* evidences the *trans* arrangement of protons H-2 and H-3. The selective INEPT method [10] was employed for the unequivocal differentiation of C-1 and C-1' signals, where after a selective excitation of the H-3 proton a nitrile group signal appeared at $\delta = 119.7$ ppm. This method was used also for assignment of signals of carbons C-1' and CN of acid *XI*. (*2E*)-Arrangement of this compound is backed by the measured coupling constants $^3J(\text{H-3}, \text{CN}) = 12.5$ Hz and $^3J(\text{H-3}, \text{COOH}) = 7.0$ Hz. Whereas compound *VIII* is a condensation product of the carbonyl group of chalcone *II* with the malonodinitrile, compound *IX* could be considered a product of retrogressive Michael addition [11]. Formation of an adduct *XII* is presumed in the first step of this reaction; under the given reaction conditions *XII* can appear in some mesomeric forms as *e.g.* *XIII* and *XIV*, which are unstable at higher temperatures and decompose to form compound *IX* according to the proposed direction.

The reaction of the chalcone *II* with methyl cyanoacetate in alkaline medium analogically gave a mixture of geometric isomers of 2-cyanocinnamic acid; its (*2Z*) isomer is unstable, and decarboxylates and, therefore, only the nitrile *X* and (*2E*)-acid *XI* were isolated from the reaction medium.

Experimental

The melting points were determined on a Kofler micro hot-stage, the UV spectra were run with Specord UVVIS (Zeiss, Jena), the IR spectra were recorded with a Perkin-Elmer, model 457 spectrophotometer, the mass spectra were recorded with JMS-100 D (Jeol) apparatus at 70 eV ionization chamber energy. Signals of ^1H and ^{13}C NMR spectra of CDCl_3 solutions measured with Bruker AM-300 apparatus at 30°C are relative to tetramethylsilane. The reactions were monitored and the purity of compounds was checked on Silufol UV 254 sheets in chloroform-ethyl acetate-heptane (volume ratio $\varphi = 1 : 2 : 2$, S_1) and chloroform-ethyl acetate-heptane-ammonia ($\varphi = 15 : 30 : 30 : 1$, S_2) and chloroform (S_3).



4-(4-*N,N*-Dimethylaminophenyl)-5-nitro-2-pentanone (III)

Nitromethane (45.2 g; 740 mmol) was added to 4-(4-*N,N*-dimethylaminophenyl)-3-buten-2-one (II) (10.0 g; 53 mmol) in methanol (100 cm³) containing sodium metal (0.5 g). The mixture was refluxed for 6 h, methanol was removed and the residue was crystallized from acetone—water ($\varphi = 1:1$) to yield 6.5 g (49%) of III, m.p. = 108—109°C, $R_f = 0.46$ (S_1). For C₁₃H₁₈N₂O₃ ($M_r = 250.3$) w_i (calc.): 62.40% C, 7.20% H, 11.20% N; w_i (found): 63.15% C, 7.46% H, 11.26% N. UV spectrum (methanol), $\lambda_{\text{max}}/\text{nm}$ (log $\{\epsilon\}$): 258 (4.13). IR spectrum, $\tilde{\nu}/\text{cm}^{-1}$: 3000, 2890, 2810, 1715, 1613, 1550, 1526, 1435. ¹H NMR spectrum, δ/ppm (CDCl₃): 7.07 (2H, d, C-2'—H + C-6'—H), $J_{2,3} = J_{5,6} = 8.5$ Hz, 6.66 (2H, d, C-3'—H + C-5'—H), 4.65 (1H, m, C-5a—H), $J_{4,5a} = 7.0$ Hz, $J_{5a,5b} = 12.0$ Hz, 4.55 (1H, m, C-5b—H), 3.91 (1H, m, C-4—H), $J_{3,4} = J_{4,5a} = 7.0$ Hz, $J_{4,5b} = 7.2$ Hz, 2.94 (6H, s, N(CH₃)₂), 2.87 (2H, d, C-3—H), $J_{3,4} = 7.0$ Hz, 2.11 (3H, s, C-1—H). Mass spectrum (m/z ($I_r/\%$)): 250 (31), 203 (69), 189 (12), 162 (41), 146 (100), 133 (14).

2-Methyl-2-[2-(4-N,N-dimethylaminophenyl)-3-nitropropyl]-1,3-dioxolane (IV)

p-Toluenesulfonic acid (2.9 g; 17 mmol) and ethylene glycol (2.8 g; 45 mmol) were added to solution of *III* (4.0 g; 16 mmol) in chloroform (150 cm³). The mixture was refluxed, the water having been simultaneously removed, cooled, the chloroform layer was washed with a NaHCO₃ solution, water, dried with sodium sulfate and evaporated. The residue was crystallized from benzene—heptane ($\varphi = 1/10$). Yield = 3.4 g (72%) of *IV*, m.p. = 78–81°C, $R_f = 0.71$ (*S*₁). For C₁₅H₂₂N₂O₄ ($M_r = 294.3$) w_i (calc.): 61.22% C, 7.48% H, 9.53% N; w_i (found): 61.95% C, 7.56% H, 9.83% N. UV spectrum (methanol), λ_{\max}/nm (log $\{\epsilon\}$): 255 (4.07). IR spectrum (chloroform), $\tilde{\nu}/\text{cm}^{-1}$: 3025, 3000, 2880, 1615, 1550, 1520, 1445, 1200, 1170, 950, 820. ¹H NMR spectrum, δ/ppm (CDCl₃): 7.08 (2H, d, C-2''—H + C-6''—H), $J_{2',3'} = J_{5',6'} = 8.5$ Hz, 6.68 (2H, d, C-3''—H + C-5''—H), 4.83 (1H, dd, C-3'a—H), $J_{2',3'a} = 6.0$ Hz, $J_{3'a,3'b} = 12.0$ Hz, 4.47 (1H, dd, C-3'b—H), $J_{2',3'b} = 9.5$ Hz, 3.95 (4H, s, C-4—H + C-5—H), 3.63 (1H, m, C-2'—H), 2.94 (6H, s, N(CH₃)₂), 2.08 + 2.03 (2H, m, C-1'a—H + C-1'b—H) $J_{1'a,1'b} = 14.5$ Hz, $J_{2',1'a} = 5.2$ Hz, 1.24 (3H, s, CH₃). Mass spectrum (m/z ($I_r/\%$)): 294 (17), 279 (1), 250 (43), 204 (13), 203 (54), 161 (24), 160 (25), 148 (38), 147 (100).

2-Methyl-2-[2-(4-N,N-dimethylaminophenyl)-3-aminopropyl]-1,3-dioxolane (V)

A solution of *IV* (2.0 g; 7 mmol) in tetrahydrofuran (50 cm³) was added to a suspension of lithium tetrahydridoaluminate (1.8 g; 47 mmol) in tetrahydrofuran (50 cm³) at –12°C. The mixture was allowed to get the room temperature and then it was refluxed for 1 h. The unreacted aluminate was decomposed by addition of water, the mixture was made alkaline to pH = 9, the separated precipitate was filtered off and heptane (15 cm³) was added to the filtrate. Concentration of the solution afforded 1.4 g (87%) of the brown amorphous substance *V*, which was characterized as the acetate *VI* prepared by acetylation in acetic anhydride—pyridine mixture. M.p. = 59–61°C (ethyl acetate). For C₁₇H₂₆N₂O₃ ($M_r = 306.4$) w_i (calc.): 66.64% C, 8.55% H, 9.14% N; w_i (found): 66.77% C, 8.48% H, 9.11% N. UV spectrum (methanol), λ_{\max}/nm (log $\{\epsilon\}$): 254 (4.02). IR spectrum (chloroform), $\tilde{\nu}/\text{cm}^{-1}$: 1710, 1670, 1610, 1520, 1445, 1225, 820. ¹H NMR spectrum, δ/ppm (CDCl₃): 7.06 (2H, d, C-2''—H + C-6''—H), $J_{2',3'} = J_{5',6'} = 8.5$ Hz, 6.63 (2H, d, C-3''—H + C-5''—H) 6.09 (1H, s, —NHCO—), 3.91 (4H, s, C-4—H + C-5—H), 3.70 (1H, m, C-2'—H), 3.10 (2H, m, C-3'—H), 2.93 (6H, s, N(CH₃)₂), 2.03 (2H, m, C-1'—H), 1.86 (3H, s, CH₃CO—), 1.21 (3H, s, CH₃). Mass spectrum (m/z ($I_r/\%$)): 306 (6), 247 (100), 206 (6), 147 (4), 144 (13), 87 (83).

4-(4-N,N-Dimethylaminophenyl)-2-methyl-1-pyrroline (I)

Compound *V* (0.5 g; 2 mmol) was stirred with hydrochloric acid (20 cm³, 3 mol/dm³) for 15 min. The pH was adjusted to 8.5 by addition of ammonia, the separated precipitate

was filtered off, the filtrate was taken into chloroform, the solvent was distilled off and the residue combined with the precipitate was crystallized from heptane. Yield = 0.38 g (83%) of *I*, m.p. = 58–60°C, $R_f = 0.22$ (S_2). For $C_{13}H_{18}N_2$ ($M_r = 202.3$) w_i (calc.): 77.19% C, 8.97% H, 13.84% N; w_i (found): 77.12% C, 9.04% H, 13.78% N. UV spectrum (methanol), λ_{max}/nm ($\log \{\epsilon\}$): 257 (4.24). IR spectrum (chloroform), $\tilde{\nu}/cm^{-1}$: 3020, 2950, 2800, 1650, 1615, 1520, 1475, 1445. 1H NMR spectrum, δ/ppm ($CDCl_3$): 7.04 (2H, d, C-2'-H + C-6'-H), $J_{2',3'} = J_{5',6'} = 8.7$ Hz, 6.68 (2H, d, C-3'-H + C-5'-H), 4.20 (1H, m, C-5a-H), $J_{5a,5b} = 15.0$ Hz, $J_{5a,4} = 8.5$ Hz, $J_{5a,3a} = 3.0$ Hz, $J_{5a,3b} = 1.7$ Hz, 3.79 (1H, m, C-5b-H), $J_{5b,4} = 6.3$ Hz, $J_{5a,3a} = 3.9$ Hz, $J_{5b,3b} = 1.9$ Hz, 3.43 (1H, m, C-4-H), $J_{4,3a} = 9.5$ Hz, $J_{4,3b} = 7.0$ Hz, 2.95 (1H, m, C-3a-H), $J_{3a,3b} = 17.0$ Hz, 2.92 (6H, s, $N(CH_3)_2$), 2.55 (1H, m, C-3b-H), 2.07 (3H, s, CH_3). Mass spectrum (m/z ($I_r/\%$)): 202 (100), 201 (31), 148 (13), 147 (96), 146 (36), 134 (9), 118 (4).

5-Amino-4-(4-*N,N*-dimethylaminophenyl)-2-pentanol (*VII*)

The procedure described for preparation of *V* was applied to synthesize *VII* as an amorphous product, m.p. = 54–60°C. For $C_{13}H_{22}N_2O$ ($M_r = 222.3$) w_i (calc.): 70.23% C, 9.97% H, 12.59% N; w_i (found): 70.15% C, 9.84% H, 12.45% N. UV spectrum (methanol), λ_{max}/nm ($\log \{\epsilon\}$): 257 (4.25). IR spectrum (chloroform), $\tilde{\nu}/cm^{-1}$: 3580, 3510, 3350, 2970, 1610, 1520, 1480. Mass spectrum (m/z ($I_r/\%$)): 222 (7), 204 (7), 193 (14), 192 (44), 176 (6), 148 (100).

(4*E*,3-*s-trans*)-5-(4'-*N,N*-Dimethylaminophenyl)-2-cyano-3-methyl-2,4-pentadienic acid nitrile (*VIII*)

A mixture of *II* (2.51 g; 13 mmol) and malonodinitrile (0.83 g) in benzene (200 cm³) was left to stand with triethylamine (1 cm³) for 24 h at an ambient temperature and then refluxed for 1 h. The solvent was evaporated and the residue was chromatographed through an alumina-packed column, chloroform–ethanol ($\phi = 99 : 1$) being the eluent. The red-coloured fraction was crystallized from chloroform–heptane ($\phi = 1 : 5$) to afford violetred crystals of *VIII*. M.p. = 220–223°C, $R_f = 0.88$ (S_3). For $C_{15}H_{15}N_3$ ($M_r = 237.3$) w_i (calc.): 75.98% C, 6.37% H, 17.70% N; w_i (found): 75.92% C, 6.25% H, 17.59% N. IR spectrum (chloroform), $\tilde{\nu}/cm^{-1}$: 2980, 2900, 2850, 2205, 1605, 1580, 1505. 1H NMR spectrum ($CDCl_3$), δ/ppm : 7.50 (2H, d, C-2'-H + C-6'-H), $J_{2',3'} = J_{5',6'} = 9.0$ Hz, 7.25 (d, 1H, C-4-H), $J_{4,5} = 15.5$ Hz, 7.19 (d, 1H, C-5-H), 6.68 (2H, d, C-3'-H + C-5'-H), 3.08 (6H, s, $N(CH_3)_2$), 2.42 (3H, s, C-3- CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ/ppm : 122.0 C-1', 131.0 C-2' + C-6', 111.9 C-3' + C-5', 152.6 C-4', 40.1 N(CH_3)₂, 114.3 C-1*, 78.5 C-2, 168.5 C-3, 118.5 C-4, 145.0 C-5, 17.6 C-3- $\underline{CH_3}$, 113.5 C-2- \underline{CN} *. Mass spectrum (m/z ($I_r/\%$)): 237 (100), 236 (40), 211 (25), 193 (6).

* May be interchanged.

4'-N,N-Dimethylamino-2-cyanocinnamic acid nitrile (IX)

The yellow fraction coming from the column when preparing *VIII* was worked up and crystallized from benzene to give 1.2 g of *IX*, m.p. = 180–182°C, $R_f = 0.82$ (S_3). For $C_{12}H_{11}N_3$ ($M_r = 197.2$) w_i (calc.): 73.08% C, 5.62% H, 21.30% N; w_i (found): 72.96% C, 5.49% H, 21.26% N. IR spectrum (chloroform), $\tilde{\nu}/\text{cm}^{-1}$: 2980, 2900, 2850, 2200, 1610, 1560, 1515, 1350, 1290, 945. ^1H NMR spectrum (CDCl_3), δ/ppm : 7.81 (2H, d, C-2'—H + C-6'—H), $J_{2',3'} = J_{5',6'} = 9.1$ Hz, 7.47 (1H, s, C-3—H), 6.69 (2H, d, C-3'—H + C-5'—H), 3.14 (6H, s, $\text{N}(\text{CH}_3)_2$). ^{13}C NMR spectrum (CDCl_3), δ/ppm : 119.2 C-1', 133.8 C-2' + C-6', 111.6 C-3' + C-5', 154.2 C-4', 40.1 $\text{N}(\text{CH}_3)_2$, 116.0 C-1, 71.6 C-2, 158.0 C-3, 114.9 C-2— $\underline{\text{CN}}$. Mass spectrum (m/z ($I_r/\%$)): 196 (100), 181 (8), 153 (8), 114 (1).

Reaction of methyl cyanoacetate with 4-(4-N,N-dimethylaminophenyl)-3-buten-2-one

Compound *II* (5.0 g; 26 mmol), methyl cyanoacetate (2.8 g; 28 mmol), and sodium methoxide (0.63 g Na; 27 mmol) in methanol (150 cm^3) were reacted at room temperature for 48 h and then refluxed for 4 h. The solvent was distilled off under reduced pressure, the residue was suspended in water and the insoluble product was filtered off and crystallized from benzene. Yield = 0.52 g of *X*, m.p. = 182–184°C, $R_f = 0.85$ (S_3). For $C_{11}H_{12}N_2$ ($M_r = 172.22$) w_i (calc.): 76.72% C, 7.02% H, 16.26% N; w_i (found): 76.64% C, 6.95% H, 16.27% N. IR spectrum (chloroform), $\tilde{\nu}/\text{cm}^{-1}$: 3040, 2900, 2880, 2200, 1590, 1520, 1480. ^1H NMR spectrum (CDCl_3), δ/ppm : 7.32 (2H, d, C-2'—H + C-6'—H), $J_{2',3'} = J_{5',6'} = 9.2$ Hz, 7.27 (1H, d, C-3—H), $J_{2,3} = 16.7$ Hz, 6.65 (2H, d, C-3'—H + C-5'—H), 5.57 (1H, d, C-2—H), 3.03 (6H, s, $\text{N}(\text{CH}_3)_2$). ^{13}C NMR spectrum (CDCl_3), δ/ppm : 121.5 C-1', 129.0 C-2' + C-6', 111.7 C-3' + C-5', 152.5 C-4', 40.1 $\text{N}(\text{CH}_3)_2$, 119.7 C-1, 89.5 C-2, 150.5 C-3. The pH of the filtrate after separation of *X* was adjusted to 6.5 by addition of acetic acid, the separated orange-coloured compound was filtered off and crystallized from ethanol. Yield = 2.2 g of *XI*, m.p. = 242–244°C, $R_f = 0.05$ (S_3). For $C_{12}H_{12}N_2O_2$ ($M_r = 216.2$) w_i (calc.): 66.67% C, 6.59% H, 12.95% N; w_i (found): 66.53% C, 6.47% H, 12.87% N. IR spectrum (KBr), $\tilde{\nu}/\text{cm}^{-1}$: 3280, 2970, 2910, 2820, 2200, 1600, 1580, 1525, 1470, 1440, 1375, 1340. ^1H NMR spectrum (CDCl_3), δ/ppm : 8.11 (1H, s, C-3—H), 7.98 (2H, d, C-2'—H + C-6'—H), $J_{2',3'} = J_{5',6'} = 9.1$ Hz, 6.71 (2H, d, C-3'—H + C-5'—H), 3.14 (6H, s, $\text{N}(\text{CH}_3)_2$). ^{13}C NMR spectrum (CDCl_3), δ/ppm : 120.1 C-1', 111.5 C-2' + C-6', 131.3 C-3' + C-5', 151.7 C-4', 164.3 C-1, 105.4 C-2, 147.9 C-3, 120.2 C-2— $\underline{\text{CN}}$. Mass spectrum (m/z ($I_r/\%$)): 216 (100), 215 (71), 172 (68), 171 (85), 156 (10), 128 (9).

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References

1. Tomko, J., Brázdová, V., and Votický, Z., *Tetrahedron Lett.* 1971, 3041.
2. Fuska, J., Fusková, A., Vassová, A., and Votický, Z., *Neoplasma* 28, 709 (1981).
3. Davey, W. and Tivey, D. J., *J. Chem. Soc.* 1958, 2276.
4. Levering, D. R., Morritz, F. L., and Lieber, E., *J. Amer. Chem. Soc.* 72, 1190 (1950).
5. Senkus, M., *J. Amer. Chem. Soc.* 69, 1380 (1947).
6. Schechter, R., Ley, D. F., and Zeldin, J., *J. Amer. Chem. Soc.* 74, 3664 (1952).
7. Kühn, L. P., *J. Amer. Chem. Soc.* 73, 1510 (1951).
8. Vincze, I., *Chem. Biotechnol. Biol. Nat. Prod.* 1983, 299.
9. Bax, A. and Freeman, R., *J. Magn. Resonance* 44, 542 (1981).
10. Bax, A., *J. Magn. Resonance* 57, 314 (1984).
11. Bergmann, E. D., Ginsburg, D., and Pappo, R., *Org. React.* 10, 179 (1959).

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