Furan derivatives
217. Synthesis and spectral properties of derivatives of 5-cyano-2-furaldehyde

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Knoevenagel condensation of 5-cyano-2-furaldehyde with propanedinitrile, amide of the cyanoacetic acid, methylcyanoacetate, 3-(2-furyl)-3--oxopropanenitrile, and 3-(4-methylphenyl)-3-oxopropanenitrile containing an active cyanomethylene group furnished the corresponding cyanoethylenes. Reaction of 5-cyano-2-furaldehyde with ethyl 3-oxobutanoate and 2,4-pentanedione gave ethyl 2-(5-cyano-2-furylidene)-3-oxobutanoate and 3-(5-cyano-2-furylidene)-2,4-pentanedione, respectively. Cyclocondensation of 5-cyano-2-furaldehyde with 3-amino-2-butenenitrile and 4-amino-3--pentene-2-one in the presence of ethanolic hydrogen chloride produced 4-(5-cyano-2-furyl)-2,6-dimethyl-1,4-dihydropyridines. The structure—spectral properties relationship of the synthesized substituted 5-cyano-2--furylethylenes and 4-(5-cyano-2-furyl)-2,6-dimethyl-1,4-dihydropyridines is discussed.

Посредством конденсации по Кневенагелю 5-циано-2-фуральдегида с пропандинитрилом, амидом цианоуксусной кислоты, метиловым эфиром цианоуксусной кислоты, 3-(2-фурил)-3-оксопропаннитрилом и 3-(4-метилфенил)-3-оксопропаннитрилом, содержащими активную цианометиленовую группу, были получены соответствующие цианоэтилены. В результате реакции с этил-3-оксобутаноатом и 2,4-пентандионом образуются этил-2-(5-циано-2-фурилиден)-3-оксобутаноат и 3-(5-циано-2-фурилиден)-2,4-пентандион. Циклоконденсация 5-циано-2-фуральдегида с 3-амино-2-бутеннитрилом и 4-амино-3-пентен-2--оном в присутствии хлористого водорода в этиловом спирте приводит к образованию 4-(5-циано-2-фурил)-2,6-диметил-1,4-дигидропиридинов. Обсуждается взаимосвязь между строением синтезированных замещенных 5-циано-2-фурилэтиленов и 4-(5-циано-2-фурил)-2,6--диметил-1,4-дигидропиридинов и их спектральными свойствами.

Despite the high reactivity of 5-cyano-2-furaldehyde its condensation has only been studied with amines [1, 2], giving potentially biologically active

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Table 1

Substituted 5-cyano-2-furylethylene derivatives *II—IV*

Compound	R	Formula	M_r	w_i(calc.)/% w_i(found)/%			Yield	M.p.[a]
				C	H	N	%	°C
IIa	CN	$C_9H_3N_3O$	169.15	63.90	1.79	24.85	75	128—130
				63.75	1.77	24.69		
IIb	$CONH_2$	$C_9H_5N_3O_2$	187.17	57.75	2.70	22.46	58	183—186
				57.65	2.68	22.40		
IIc	CO_2CH_3	$C_{10}H_6N_2O_3$	202.18	59.40	3.00	13.86	66	165—167
				59.29	2.97	13.68		
IId	$2-C_4H_3O$	$C_{13}H_6N_2O_3$	238.21	65.54	2.54	11.76	51	168—171
				65.48	2.50	11.60		
IIe	$p-CH_3C_6H_4CO$	$C_{16}H_{10}N_2O_2$	262.28	73.27	3.85	10.68	69	159—161
				73.18	3.80	10.58		
III	$CO_2C_2H_5$	$C_{12}H_{11}NO_4$	233.24	61.79	4.79	6.01	57	98—101
				61.72	4.71	5.90		
IV	CH_3CO	$C_{11}H_9NO_3$	203.21	65.01	4.47	6.89	48	92—93
				65.10	4.44	6.73		

a) Crystallized from ethanol; compounds *IIb—IIe* from a toluene—ethanol mixture.

products. Condensation with compounds having an active methylene group have not yet been described.

Now we report on the utilization of 5-cyano-2-furaldehyde in the synthesis of activated ethylene derivatives as well as some 1,4-dihydropyridines. At the same time the cyano group in position 5 of the furan ring served as a model of an electronwithdrawing substituent in correlating spectral properties with Hammett constants.

The starting 5-cyano-2-furaldehyde was prepared by the reaction of 5-iodo-2--furaldehyde with copper(I) cyanide according to [1]. Modified Knoevenagel condensation with propanedinitrile (*Ia*), cyanoacetic acid amide (*Ib*), and 3-(4--methylphenyl)-3-oxopropanenitrile (*Ie*) furnished in good yields the corresponding 2-(5-cyano-2-furyl)-1-cyanoethylenes *IIa—IIe* (Table 1). The reaction proceeded without the catalyst. In the preparation of acetylethylenes *III* and *IV* glycine was used as catalyst.

In modified Hantzsch procedure cyclocondensation of 5-cyano-2-fural-dehyde with 3-amino-2-butenenitrile (*Va*) in the presence of ethanolic hydrogen chloride solution gave rise to 3,5-dicyano-2,6-dimethyl-1,4-dihydropyridine (*VIa*) in 56 % yield. Diacetyl derivative 3,5-diacetyl-4-(2-furyl)-2,6-dimethyl--1,4-dihydropyridine (*VIb*) was prepared in similar manner starting from 4--amino-3-pentene-2-one (*Vb*).

Ultraviolet spectra of cyanoethylenes *IIa—IIe* displayed in the region 200—400 nm (Table 2) two absorption bands at $\lambda_{max} = 212$—218 nm (log $(\varepsilon/$ $/(m^2 \text{ mol}^{-1})) = 3.02$—3.23) and at $\lambda_{max} = 326$—351 nm (log $(\varepsilon/(m^2 \text{ mol}^{-1})) =$ $= 3.34$—3.44). Compounds *IId* and *IIe* showed an additional maximum at $\lambda_{max} = 243$ nm (*IId*) and $\lambda_{max} = 232$ nm (*IIe*), attributed to the furyl and *p*-tolyl chromophore, respectively. Position of the longwave maximum corresponding to the $\pi \rightarrow \pi^*$ transition of the whole conjugated system was significantly influenced by substituent R. Bathochromic shift of λ_{max} of the compounds *IId* ($\Delta\lambda_{max} = 15$ nm) and *IIe* ($\Delta\lambda_{max} = 3$ nm) with respect to *IIa* was caused presumably by the extention of the conjugated system, when the cyano group was substituted by an aroyl substituent. In acetylethylenes *III* and *IV* the exchange of the ethoxycarbonyl group for an acetyl did not alter the shape of the absorption curve of the UV spectra.

Infrared spectra of 2-furylethylenes *II—IV* (Table 2) displayed absorption maxima of stretching vibrations of the CN group at $\tilde{\nu} = 2213$—2233 cm^{-1}. In the IR spectra of *IIa* and *IIb* the bands of both cyano groups overlap, so that only one maximum can be observed. Cyanoethylenes *IIc—IIe* showed in this region two absorption bands. Comparison with derivatives *III* and *IV*, possessing only the cyano group in the position 5 of the furan ring enabled us to assign the peak at lower wavenumbers ($\tilde{\nu} = 2213$—2219 cm^{-1}) to the cyano group at

Table 2

IR and UV spectra of 5-cyano-2-furylethylene derivatives *II—IV*

Compound	$\dfrac{\lambda_{max}{}^a}{nm}$	$\log(\varepsilon/(m^2\,mol^{-1}))$	$\tilde{\nu}_{max}(KBr)/cm^{-1}$			
			$\nu(C{\equiv}N)$	$\nu(C{=}C)$		$\nu(R)^b$
IIa	218	3.15	2230	1601	1474	—
	336	3.44		1534	1368	
IIb	217	3.09	2220	1612	1484	1681
	326	3.41		1548	1385	
IIc	218	3.06	2219	1602	1432	1723
	332	3.38	2233	1482	1364	
IId	217	3.02	2213	1572	1454	1654
	243	2.90	2230	1556	1387	
	351	3.34		1481		
IIe	212	3.23	2214	1602	1404	1660
	232	3.00	2226	1544	1374	
	339	3.40		1490		
III	214	3.05	2227	1624	1466	1727
	311	3.34		1550	1445	1658^c
	317 sh	3.32		1481	1372	
IV	218	3.11	2227	1614	1434	1710
	311	3.41		1481	1366	1656^c
	319 sh	3.40				

a) Methanol ($c = 5 \times 10^{-5}\,mol\,dm^{-3}$); *b*) $\nu(C{=}O)$; *c*) $\nu(C{=}O)$ of the CH_3CO group. sh — shoulder.

Table 3

^1H NMR spectra of 5-cyano-2-furylethylene derivatives *II—IV*

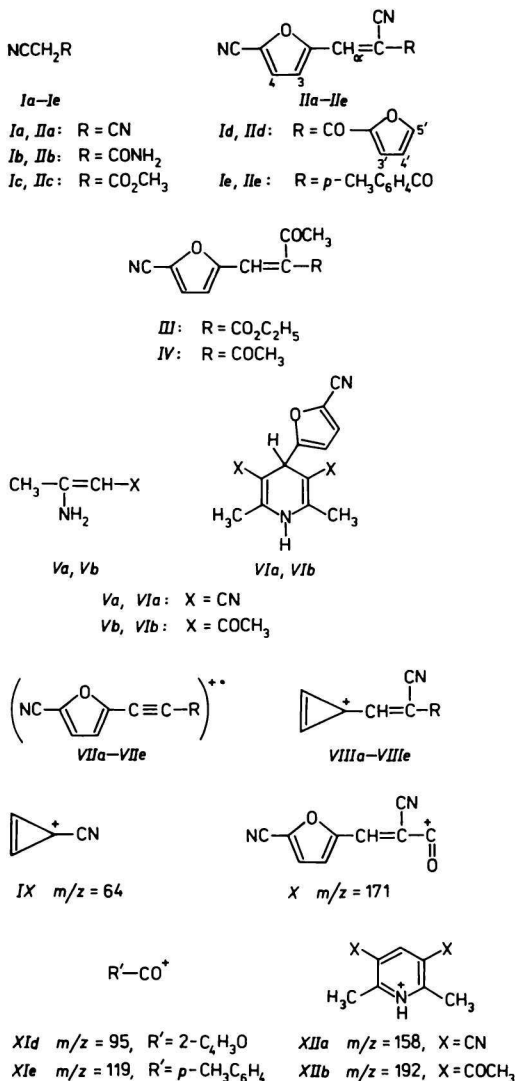| Compound	$\delta(H)/ppm^a$			
	H-3 (d)	H-4 (d)^b	H (s)	R
IIa	7.50	7.83	8.40	—
IIb	7.41	7.74	7.98	7.86 broad s (NH_2)
IIc	7.54	7.79	8.20	3.83 s (CH_3)
IId	7.60	7.84	8.25	6.83 m (H-4′), 7.70 dd (H-3′), 8.16 m (H-5′)
IIe	7.53	7.79	7.93	7.72 d (H_{ortho})^c, 7.34 d (H_{meta})^c, 2.35 s (CH_3)
III^d	7.17	7.68	7.61	1.22 t (CH_3), 4.25 q (OCH_2)
IV^d	7.08	7.65	7.46	2.29 s (CH_3)

a) Measured in deuterated dimethyl sulfoxide at 25 °C; *b*) $^3J(H-3, H-4) = 3.8\,Hz$; *c*) position with respect to the carbonyl group, $^3J = 8.2\,Hz$; *d*) 2.34 (s, 3H, CH_3CO).

the acyclic double bond. In the region $\tilde{\nu} = 1364$—$1624\,\mathrm{cm}^{-1}$ stretching vibrations of the furan ring and those of C=C bond are located [3].

Dihydropyridines *VI* showed in their IR spectra absorption bands belonging to the stretching vibrations of NH, CN, and CO groups (compound *VIb*). Absorption maxima at $\tilde{\nu} = 1655\,\mathrm{cm}^{-1}$ (*VIa*) and $\tilde{\nu} = 1665\,\mathrm{cm}^{-1}$ (*VIb*) are characteristic of 1,4-dihydropyridine skeleton [4, 5]. In contrast to *VIa*, IR spectrum of *VIb* displayed an intensive band at $\tilde{\nu} = 1594\,\mathrm{cm}^{-1}$, corresponding probably to the stretching vibrations of carbonyl groups of acetyl substituents, strongly conjugated with the 1,4-dihydropyridine skeleton. Effective conjugation in *VIb* is also manifested by a bathochromic shift of λ_{max} by 30 nm as well as by the difference in chemical shift of the H—C-4 proton $\Delta\delta = 0.64\,\mathrm{ppm}$ compared with that in 3,5-dicyano-1,4-dihydropyridine *VIa*. ^{1}H NMR spectra (Table 3) are in accord with the structures *II—IV* and betray the presence of only one isomer. Similarity of the spectra of *IIa—IIe* with those of analogous 5-substituted 2-furylethylenes [6] and 2-arylidene-3-oxopropanenitriles [7] has led to the assumption, that compounds *IIa—IIe* are *E* isomers, H$_a$ and CN group being in *trans* position. Measured values of vicinal splitting constants $^3J(\mathrm{HCN}) = 14\,\mathrm{Hz}$ and $^3J(\mathrm{HCO}) = 6.1\,\mathrm{Hz}$ support the assignment. Doublets of furan ring protons were observed at $J_i = 7.08$—$7.60\,\mathrm{Hz}$ (H-3) and $J_i = 7.65$—$7.84\,\mathrm{Hz}$ (H-4). As can be seen from data in Table 3 H$_a$ was most influenced by the substituent R. Dicyanoethylene *IIa* displayed the highest downfield shift, the effect of R abates in the order *IIa*, *IId*, *IIc*, *IIb*, *IIe* tallying with electronacceptor properties of the substituent R in position β at the double bond. Exchanging an ethoxycarbonyl group (derivative *III*) for an acetyl (derivative *IV*) caused a downfield shift of H$_a$ as well. 2,4-Pentanedione derivative *IV* showed signals of both nonequivalent acetyl groups in contrast to [8], where the authors gave only one value for COCH$_3$ groups of 5-substituted 2-furylmethylene-2,4--pentanediones. In ^{1}H NMR spectra of *VIb* (X = COCH$_3$) signals of furan ring protons H-3' and H-4' unlike those of *VIa* (X = CN), were doublets of doublets, testifying to their interaction with H-4 of the 1,4-dihydropyridine skeleton ($^4J(\mathrm{H}\text{-}3', \mathrm{H}\text{-}4) = 0.7\,\mathrm{Hz}$, $^5J(\mathrm{H}\text{-}4', \mathrm{H}\text{-}4) = 0.3\,\mathrm{Hz}$). This effect can be accounted for by different conformation of the furan ring with respect to 1,4-dihydropyridine, enforced by bulky acetyl groups in positions 3 and 5 of the compound *VIb*.

Ionic species found in mass spectra of *II*, *III*, and *VI* are described in Experimental, basic fragments are given in Scheme 1. Molecular ions, base peaks in spectra of *IIa—IIc*, were in compounds of the type *II* split by three alternative processes. A fragmentation common for all compounds *II* encompasses an elimination of HCN, giving rise to *VII*$^{+\bullet}$. In the following minor process CO and NC$^\bullet$ are further lost from the furan ring to give *VIII*$^+$.. m/z

Values and relative intensities of the observed ions depend on the character of R. Ion $VIII^+$ suffers further fragmentation to IX^+, $m/z = 64$, common for all derivatives II. Fragment ions of the type $VIII^+$ and IX^+ are characteristic of all furan derivatives [9—11]. The third fragmenting process is specific for every 5-cyano-2- furylethylene of the type II. Thus IIb and IIc eliminated $H_2N^\bullet$ radical (IIb) and $H_3CO^\bullet$ (IIc) to give identical fragment ion X^+, $m/z = 171$. Ions XI^+

$$NCCH_2R$$

Ia—Ie

Ia, IIa: R = CN
Ib, IIb: R = CONH$_2$
Ic, IIc: R = CO$_2$CH$_3$

Id, IId: R = CO—
Ie, IIe: R = p-CH$_3$C$_6$H$_4$CO

IIa—IIe

III: R = CO$_2$C$_2$H$_5$
IV: R = COCH$_3$

Va, Vb

VIa, VIb

Va, VIa: X = CN
Vb, VIb: X = COCH$_3$

VIIa—VIIe

VIIIa—VIIIe

IX $m/z = 64$

X $m/z = 171$

$$R'-CO^+$$

XId $m/z = 95$, R' = 2-C$_4$H$_3$O
XIe $m/z = 119$, R' = p-CH$_3$C$_6$H$_4$

XIIa $m/z = 158$, X = CN
XIIb $m/z = 192$, X = COCH$_3$

Scheme 1

were found to be base peaks in spectra of *IId* and *IIe*. They are characteristic of 2-arylmethylene-3-oxopropanenitriles [12]. Their further fragmentation starts with elimination of CO, as documented by metastable ions. Another fragmentation process, found in *VI*, typical for substituted 1,4-dihydropyridines [4, 5], entails a loss of substituent from C-4 to form a base peak $XIIa^+$, $m/z = 158$ and $XIIb^+$, $m/z = 192$. 1,4-Dihydropyridines *VI* were further degraded by splitting off of the radical $X^\bullet$ from position 3, $H_3C^\bullet$ from position 2, elimination of hydrogen molecule and fragmentation of the furan ring.

Experimental

Melting points were determined on a Kofler hot stage. The following spectrometers were used for spectral measurements: UR 70 (Zeiss, Jena) (IR), Specord UV VIS (Zeiss, Jena) (UV), AEI MS 902 S (HS, 70 eV). ^{1}H NMR spectra were measured with a 80 MHz spectrometer Tesla BS 487 C, using hexamethyldisiloxane as internal standard, measurements in deuterated acetone were performed with tetramethylsilane standard. ^{13}C NMR spectrum of *IId* was measured on a Jeol FX-100 spectrometer.

5-Cyano-2-furaldehyde was prepared by the action of copper(I) cyanide on 5-iodo-2--furaldehyde in dimethylformamide according to [1] in 43 % yield, b.p.(2 kPa) = 89 °C (Ref. [1] gives b.p.(2.7 kPa) = 108—110 °C.

1-R-1-Cyano-2-(5-cyano-2-furyl)ethylenes IIa—IIe

A mixture of 5-cyano-2-furaldehyde (10 mmol) and the corresponding cyano derivative *Ia—Ie* (10 mmol) in 10 cm^3 of dry ethanol was heated to 50 °C for 10 min and left to stand for 5 h at laboratory temperature. The precipitated solid was sucked off and crystallized from suitable solvent (Table 1).

^{13}C NMR spectrum, δ/ppm (deuterated dimethyl sulfoxide): *IId*: 108.1 (C_β), 110.6 (CN), 112.8 (C-4'), 115.1 (NC—C), 121.8 (C-3'), 122.0 (C-3), 125.1 (C-4), 127.9 (C-5), 137.4 (C_a), 149.2 (C-5'), 149.3 (C-2), 151.8 (C-2'), 172.2 (CO).

Mass spectrum, m/z (relative intensity/%): *IIa*: 170 (10), 169 (100) M$^{+\bullet}$, 142—141 (9—8), 115—114 (13—10), 106 (3), 90 (3), 89 (7), 88 (5), 77 (3), 64—63 (6—5), 54 (4), 51 (3). *IIb*: 188 (10), 187 (100) M$^{+\bullet}$, 172—171 (17—16), 161—160 (14—73), 159 (11), 144 (16), 143 (12), 142 (15), 133—132 (12—30), 118 (4), 117—116 (45—9), 115 (13), 105—104 (5—15), 90—89 (5—28), 88—87 (33—4), 77 (3), 65—64 (3—30), 63—62 (17—17), 61 (7), 54 (5), 53—52 (3—8), 51 (7), 50 (4). *IIc*: 203 (11), 202 (100) M$^{+\bullet}$, 201 (3), 187 (3), 176—175 (5—31), 172—171 (9—88), 170 (3), 160—159 (7—2), 148—147 (6—3), 144—143 (5—15), 142 (5), 136 (5), 132 (6), 130 (5), 117 (8), 115 (18), 96 (3), 89—88 (11—30), 87 (3), 64—63 (27—8), 62—61 (8—4), 59 (28), 54 (4), 51 (4). *IId*: 239 (8), 238 (63) M$^{+\bullet}$, 212 (8), 211—210 (6—7), 184—183 (5—4), 182 (3), 156 (4), 154 (3), 149 (7), 127 (3), 105 (3), 96—95 (6—100), 89 (6), 68—67 (4—7), 64—63 (7—3), 51 (4). *IIe*: 263 (8), 262 (43)

$M^{+\bullet}$, 247 (3), 235 (3), 206 (8), 120—119 (8—100), 118 (2), 92—91 (4—40), 89 (4), 65—64 (16—3), 63 (4), 51 (3).

1-R-1-Acetyl-2-(5-cyano-2-furyl)ethylenes III and IV

A mixture consisting of 10 mmol of 5-cyano-2-furaldehyde, 10 mmol of 3-oxobutanoate or 2,4-pentanedione, 0.15 g of glycine, 3 cm^3 of water, and 7 cm^3 of ethanol was refluxed for 3 h, then left to stand for 12 h at laboratory temperature. The precipitated solid was separated and crystallized from ethanol (Table 1).

Mass spectrum, m/z (relative intensity/%): *III*: 234 (8), 233 (58) $M^{+\bullet}$, 219—218 (25——21), 207—206 (9—72), 205—204 (4—21), 190—189 (18—3), 188—187 (25—6), 179——178 (3—22), 174 (3), 162—161 (5—4), 159—158 (5—3), 150—149 (10—3), 147 (6), 146——145 (58—5), 144 (3), 136 (15), 134 (5), 122 (5), 119—118 (6—14), 117 (4), 91—90 (3—6), 89 (4), 77 (4), 64—63 (5—19), 62 (6), 53 (4), 51 (4).

3,5-Disubstituted 2,6-dimethyl-4-(5-cyano-2-furyl)-1,4-dihydropyridines VIa and VIb

To the stirred solution of 5-cyano-2-furaldehyde (10 mmol) and enamine *V* (20 mmol) in 20 cm^3 of ethanol was added a solution of dry hydrogen chloride (a 5 % solution in dry ethanol) until the reaction mixture was acidic (pH = 3—4). The mixture was then heated to its boiling point for 15 min and left to stand for 12 h at laboratory temperature. It was then decomposed by the addition of 200 cm^3 of water. The separated dihydro derivative *VI* was filtered off, washed with 5 % NaOH (20 cm^3), then with water till neutral reaction.

3,5-Dicyano derivative VIa: yield = 56 %, m.p. = 218—220 °C (ethanol). For $C_{14}H_{10}N_4O$ ($M_r = 250.28$) w_i(calc.): 67.18 % C, 4.04 % H, 22.39 % N; w_i(found): 67.02 % C, 4.01 % H, 22.25 % N. UV spectrum (methanol), λ_{max}/nm (log (ε/ /(m^2 mol^{-1}))): 218 (3.34), 256 (3.19), 344 (2.83). IR spectrum (KBr), $\tilde{\nu}$/cm^{-1}: 3277, 3217 ($\tilde{\nu}$(NH)), 2205 ($\tilde{\nu}$(CN)), 1655, 1508, 1430 (1,4-dihydropyridine and furan skeleton). ^{1}H NMR spectrum (C^{2}H$_3$COC^{2}H$_3$), δ/ppm: 2.15 (s, 6H, 2 × CH$_3$), 4.75 (s, 1H, H—C-4), 6.63 (d, 1H, H-3'), 7.42 (d, 1H, H-4', $^3J = 3.8$ Hz), 8.79 (broad s, 1H, NH). Mass spectrum, m/z (relative intensity/%): 251 (11), 250 (65) $M^{+\bullet}$, 249—248 (55—36), 236—235 (9—58), 224—223 (9—6), 222—221 (27—17), 218 (4), 215 (3), 197—196 (9—61), 195—194 (9 —9), 193 (5), 181—180 (7—5), 169—168 (3—3), 167 (3), 159—158 (11—100), 157—156 (20—7), 153—152 (5—3), 144—143 (4—5), 142 (4), 140 (5), 131—130 (5—3), 129 (4), 126 (4), 125 (5), 117 (4), 116—115 (3—4), 114 (3), 104—103 (5—3), 102 (4), 100 (3), 90 (6), 89—88 (4—6), 78—77 (3—6), 76—75 (4—3), 65—64 (4—10), 63—62 (7—3), 52—51 (3 —5).

3,5-Diacetyl derivative VIb: yield = 60 %, m.p. = 172—173 °C (toluene). For $C_{16}H_{16}N_2O_3$ ($M_r = 284.34$) w_i(calc.): 67.58 % C, 5.68 % H, 9.85 % N; w_i(found):

67.43 % C, 5.51 % H, 9.75 % N. UV spectrum (methanol), λ_{max}/nm (log (ε/(m^2 mol^{-1}))): 252 (3.47), 374 (3.00). IR spectrum (KBr), $\tilde{v}$/cm^{-1}: 3290 ($\tilde{v}$(NH)), 2226 ($\tilde{v}$(CN)), 1665, 1594, 1509, 1454, 1377 (1,4-dihydropyridine and furan skeleton). ^{1}H NMR spectrum (C^{2}H$_3$COC^{2}H$_3$), δ/ppm: 2.33 (s, 6H, 2 × CH$_3$), 2.35 (s, 6H, 2 × COCH$_3$), 5.39 (m, 1H, H—C-4), 6.21 (dd, 1H, H-3′, ^3J(H-3′, H-4′) = 3.8 Hz, ^4J(H-3′, H-4) = 0.7 Hz), 7.22 (dd, 1H, H-4′, ^5J(H-4′, H-4) = 0.3 Hz), 8.29 (broad s, 1H, NH). Mass spectrum, m/z (relative intensity/%): *VIb*: 285 (12), 284 (66) M$^{+\bullet}$, 283—282 (7—3), 269 (13), 256 (5), 243—242 (5—38), 241 (100), 231—230 (7—44), 228—227 (4—10), 225 (4), 223 (3), 216—215 (8—38), 214—213 (38—7), 200 (7), 199—198 (17—5), 197 (4), 193—192 (4—31), 191 (5), 188—187 (9—4), 186 (7), 176 (10), 174—173 (3—4), 172—171 (5—4), 170—169 (3—4), 158 (4), 150—149 (5—11), 148 (6), 145—144 (3—6), 143 (3), 136 (6), 134 (8), 120 (3), 115 (4), 108—107 (3—6), 106 (11), 93—92 (5—25), 91 (38), 89 (4), 79 (4), 77 (7), 67 (8), 65—64 (9—3), 63 (6), 51—50 (7—3).

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