SYNTHESIS AND SPECTRAL PROPERTIES OF PYRROLO[3',4' : 5,6]-4*H*-PYRANO[2,3-*d*]PYRIMIDINE DERIVATIVES

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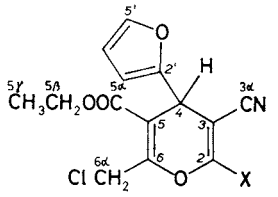
The starting 2-amino-5-ethoxycarbonyl-6-chloromethyl-4-(2-furyl)-3-cyano-4*H*-pyran (*I*) afforded on condensation with triethoxymethane 2-ethoxymethylenamino-4*H*-pyran *II*; treatment of the latter with ammonia yielded 2-formamidino-3-cyano-4*H*-pyran *III*, which, when heated in dilute ethanol, cyclized to 4-amino-6-ethoxycarbonyl-5-(2-furyl)-7-chloromethyl-4*H*-pyrano[2,3-*d*]-pyrimidine (*IV*). Compound *IV* reacted with alkyl- or arylamines to give substituted 5*H*,6*H*,8*H*-pyrrolo[3',4' : 5,6]-4*H*-pyrano[2,3-*d*]pyrimidines *VI*, one of which (*VIb*, R = *p*-$CH_3C_6H_4$) was alternatively obtained from 2-formamidino-4*H*-pyrano derivative *III*. The structures of new tricyclic heterocycles were corroborated by analysis of the NMR spectral data.

Although substituted 2-amino-3-cyano-4*H*-pyrans are well accessible[1-4], only few syntheses of fused heterocycles containing the 4*H*-pyran ring have made use of them. Thus, treatment with trichloroacetonitrile[5], ethyl 3-amino-2-cyano-4,4,4-trichloro-2-butenoate[5], or triethoxymethane and ammonia[6,7] afforded pyrano[2,3-*d*]-pyrimidines; 2-amino-3-cyano-4*H*-pyrans react with malononitrile and hydrazine hydrate to give pyrano[2,3-*b*]pyridines and 4-pyrano[2,3-*c*]pyrazoles[5], respectively. This paper presents the utilization of 2-amino-5-ethoxycarbonyl-6-chloromethyl-4-(2-furyl)-3-cyano-4*H*-pyran (*I*) as a synthon for obtaining derivatives of pyrrolo-[3',4' : 5, 6]-4*H*-pyrano[2,3-*d*]pyrimidine, which represents a new tricyclic heterocycle.

The starting 4*H*-pyran *I*, an advantageous synthon for further functional modifications of the 4*H*-pyran side chain, was prepared by a morpholine catalyzed reaction of 2-furfurylidenepropanedinitrile with ethyl 4-chloro-3-oxobutanoate. First of all, the pyrimidine ring was fused to 4*H*-pyran by an analogous procedure as reported for substituted 2-amino-4-(2-furyl)-3-cyano-4*H*-pyrans[6]. In this way, 4*H*-pyran *I* was condensed with triethoxymethane to give 2-ethoxymethylenamino-4*H*-pyran *II* (73% yield), which reacted with ammonia to afford 2-formamidino-4*H*-pyran *III*. Heating of *III* in dilute ethanol (50%) led to an intramolecular cyclization to 4*H*-pyrano[2,3-*d*]pyrimidine *IV* in 70% yield. Cyclocondensation of *IV* with alkyl- or

arylamines furnished N-substituted 5-(2-furyl)-5*H*,6*H*,8*H*-pyrrolo[3′,4′ : 5,6]-4*H*--pyrano[2,3-*d*]pyrimidin-6-ones *VI* in 46–52% yields.

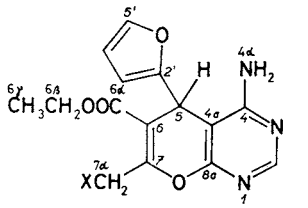
Compound *VIb* (R = *p*-$CH_3C_6H_4$) was alternatively synthesized from 2-formamidino-3-cyano-4*H*-pyran *III* and *p*-toluidine. The nucleophilic substitution of chlorine in the chloromethyl group in the presence of potassium carbonate in acetonitrile was accompanied by cyclization at the other side chain to form 4*H*-pyrano[2,3-*d*]pyrimidine *V*. As known, heterocyclic 2-formamidino-3-cyano derivatives of type *III* easily undergo cyclization in alkaline medium creating a pyrimidine ring[8]. On heating in dimethylformamide, compound *V* gave pyrrolo[3′,4′ : 5,6]-4*H*-pyrano[2,3-*d*]pyrimidin-6-one (*VIb*) identical with that prepared from compound *IV* and *p*-toluidine. This procedure is disadvantageous because of a low yield (39%) of 4*H*-pyrano[2,3-*d*]pyrimidine *V* and a purification necessity (column chromatography) prior to cyclization.



I, X = $\overset{2\alpha}{NH_2}$

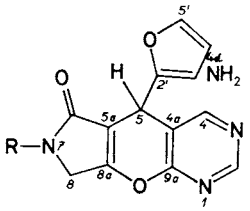
II, X = $\overset{2\alpha}{N}=\overset{2\beta}{CH}-O-\overset{2\gamma}{CH_2}-\overset{2\delta}{CH_3}$

III, X = $\overset{2\alpha}{N}=\overset{2\beta}{CH}-\overset{2\gamma}{NH_2}$



IV, X = Cl

V, X = $\overset{7\beta}{NH}$–C$_6$H$_4$–$\overset{5}{CH_3}$



VI a, R = C_6H_5

VI b, R = C$_6$H$_4$–$\overset{5}{CH_3}$

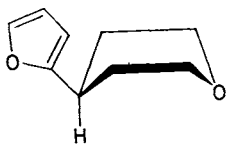
VI c, R = $\overset{7\alpha}{CH_2}$–C$_6$H$_4$

VI d, R = $\overset{7\alpha}{CH_2}\overset{7\beta}{CH_2}\overset{7\gamma}{CH_2}\overset{7\delta}{CH_3}$

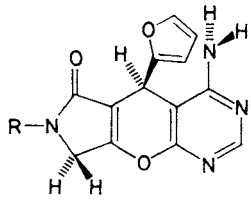
Elemental analyses and spectral data of compounds synthesized are in line with requirements for formulas *I*–*VI*. The IR spectra of compounds *VI* show characteristic absorptions of the particular functional groups at 3 320–3 413 cm^{-1} (NH_2), 1 699–1 708 cm^{-1} (CO) and 1 500–1 690 cm^{-1} (strong, C=C). The tricyclic

heterocyclic chromophore of these compounds is associated with three indicative absorptions in their UV spectra at 200–214, 227–259 and 256–275 nm.

The ^{1}H NMR data of compounds *I*–*VI* listed in Tables I–III offer following information on the structure. The proton at the chiral centre of the molecule is H-4 in compounds *I*–*III* or H-5 in *IV*–*VI*. It appears as a singlet in compounds *I*–*V*, and its chemical shift value strongly depends on the electronegativity of the substituent in position 2 of the 4*H*-pyran ring. The paramagnetic shift value increased up to $\Delta\delta = 0{\cdot}72$ ppm due to closure of the pyrimidine ring (conversion of compound *I* to *IV*). Closure of the further, lactam ring (leading to compounds *VI*), was manifested both by a decrease of this shift by approximately 0·1 ppm and splitting the singlet into a doublet as a result of interaction with the H-8 proton of the CH_2 group. This homoallylic transoid splitting[9] through 5 bonds ($^5J = 1{\cdot}5$ Hz) is in accordance with the proposed structure of the 4*H*-pyran skeleton in a boat form with H-5 in the pseudoaxial position and the 2-furyl grouping in a pseudoequatorial position (cf. formulae *A* and *B*). This long-range interaction is due to planarity of the five-membered lactam ring with rigid protons of the CH_2 group.



A



B

TABLE I

^{1}H and ^{13}C NMR data of the 2-furyl substituent of compounds *I*–*VI*

Compound	^{1}H NMR[a]			^{13}C NMR			
	H-3′	H-4′	H-5′	C-2′	C-3′	C-4′	C-5′
I	6·14 dd	6·37 dd	7·55 dd	154·96	105·80	110·49	142·42
II	6·29 dd	6·43 dd	7·62 dd	153·19	107·16	110·76	143·11
III	6·19 dd	6·39 dd	7·57 dd	154·92	106·32	110·57	142·62
IV	6·36 dd	6·34 dd	7·49 dd	152·63	107·23	110·30	142·56
V	6·26 dd	6·31 dd	7·44 dd	153·41	106·74	110·19	142·22
VIb	6·48 dd	6·36 dd	7·49 dd	151·83	107·60	110·30	142·29
VIc	6·45 dd	6·36 dd	7·49 dd	152·08	107·41	110·30	142·26
VId	6·42 dd	6·34 dd	7·46 dd	152·17	107·32	110·27	142·20

[a] ^3J(H3′, H4′) = 3·2 Hz; ^3J(H4′, H5′) = 1·8 Hz; ^4J(H3′, H5′) = 0·8 Hz.

The proposed structure is also in line with the ^{1}H NMR chemical shifts of protons at the 2-furyl grouping, which values decrease in the order H-3′ > H-4′ > H-5′ (cf. Table I); it follows that the furan ring is in a perpendicular plane in respect to the 4*H*-pyran ring. The boat form of *IV*–*VI* could be backed by analogy with 2-amino-3-ethoxycarbonyl-4-(3-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran, the boat form of which in solid state was proved on the basis of X-ray diffraction analysis[10]. The above-mentioned statements were also in full accord with inspection of Dreiding models.

The C-4 and C-5 chiralities in compounds *I*–*VI* indicate prochiral properties of the CH_2 protons at C-5β, C-6β, C-6α, and C-7α in *I*–*V* and of protons H-8 in

TABLE II

^{1}H NMR chemical shift data of compounds *I*–*VI*

Compound	H-4	H-5β	H-5γ	H-6α	H-6β	H-2β	NH_2	Others
I	4·55 s	4·13 m	1·16 t	4·65 d	4·78 d	—	7·19 s (2 H)	—
II	4·82 s	4·13 m	1·15 t	4·76 d	4·82 d	8·57 s	—	[a]
III	4·66 s	4·12 m	1·16 t	4·75 d	4·89 d	8·19 dd	8·33 dd (1 H) 7·98 t (1 H)	—
	H-5	H-6β	H-6γ	H-7α		H-2	NH_2	Others
IV	5·27 s	4·19 m	1·25 t	4·76 d	4·89 d	8·10 s	7·17 bs	—
V	5·21 s	4·20 m	1·24 t	4·29 dd	4·51 dd	8·04 s	7·08 bs	[b]
	H-5	—	—	H-8		H-2	NH_2	Others
VIb	5·15 d	—	—	4·71 dd	4·85 d	8·13 s	7·10 bs	[c]
VIc	5·12 d	—	—	4·10 dd	4·26 d	8·10 s	7·03 bs	[d]
VId	5·07 d	—	—	4·18 dd	4·30 d	8·10 s	7·05 bs	[e]

[a] 4·33 q, 2 H (2 × H-2γ); 1·31 t, 3 H (3 × H-2δ); [b] 5·80 t, 1 H (NH-7β); 6·55 d, 2 H (2 × H-2, *p*-tolyl); 6·87 d, 2 H (2 × H-3, *p*-tolyl); 2·13 s, 3 H (3 × H-5, *p*-tolyl); [c] 7·58 d, 2 H (2 × H-2, *p*-tolyl); 7·16 d, 2 H (2 × H-3, *p*-tolyl); 2·26 s, 3 H (3 × H-5, *p*-tolyl); [d] 4·45 d, 1 H and 4·59, 1 H (2 × H-7α); 6·92 d, 2 H (2 × H-2, phenyl); 7·34 t, 2 H (2 × H-3, phenyl); 7·27 t, 1 H (H-4, phenyl); [e] 3·29 m, 2 H (2 × H-7α); 1·47 m, 2 H (2 × H-7β); 1·24 m, 2 H (2 × H-7γ); 0·87 t, 3 H (3 × H-7δ).

TABLE III

Coupling constant (J H, H) values for compounds *I*—*VI* in Hz

Compound	^2J(H-5β)	^3J(H-5β, H-5γ)	^2J(H-6α)	Others
I	10·7	7·05	11·9	—
II	10·8	7·09	11·7	^3J(H-2γ, H-2δ) = 7·1 Hz
III	10·7	7·09	11·9	^3J(H-2β, H-2γa) = 14·35 Hz ^3J(H-2β, H-2γb) = 4·75 Hz ^2J(H-2γ) = 2·2 Hz
	^2J(H-6β)	^3J(H-6β, H-6γ)	^2J(H-7α)	Others
IV	10·8	7·09	11·7	—
V	11·0	7·09	15·6	^3J(H-7α, H-7β) = 6·9 Hz, phenyl: ^3J(H-2, H-3) = 8·5 Hz
	—	—	^2J(H-8)	^5J(H-5, H-8) Others
VIb	—	—	18·0	1·45 *p*-tolyl: ^3J(H-2, H-3) = 8·6 Hz
VIc	—	—	18·6	1·45 ^2J(H-7α) = 15·5 Hz, phenyl: ^3J(H-2, H-3) = 8·5 Hz, ^3J(H-3, H-4) = 7·5 Hz
VId	—	—	18·7	1·55 ^3J(H-7γ, H-7δ) = 7·35 Hz

VI. The nonequivalence of CH_2 protons is due to a prochirality of the CH_2 group[11] and not to a hindered rotation, as evidenced by measuring the thermal dependence.

Transition from the freely rotating C-6α CH_2 group in compounds *I*–*III* and C-7α CH_2 in *IV*–*V* to a rigid CH_2 group in *VI* is associated with an increase of the geminal coupling constant ^2J by 7 Hz up to 18·7 Hz for *VId* and the already mentioned long-range coupling with H-5 proton in compounds *VI*. The ^2J value for *V* is influenced by a bulky substituent bound to CH_2. The coupling constant values ^2J and ^5J (cf. Table III) are in a good agreement with the predicted values of Karplus relationships[9,12] of coupling constants on the magnitude of dihedral angles.

The ^{13}C NMR spectral data of the 2-furyl grouping are listed in Table I, those for compounds *I*–*VI* in Table IV. Signals of quaternary carbons of the 4*H*-pyran ring were assigned according to long-range INEPT technique[13]. The most noticeable changes in chemical shift displayed the C-3 carbon in compounds *I*–*III* as a result of the change in character of the substituent attached to position 2 on conversion from *I* to *III*.

EXPERIMENTAL

The melting points were determined on a Boetius micro hot-stage, the IR ($\tilde{\nu}$, cm^{-1}) and the UV (λ, nm; (log ε, $m^2\ mol^{-1}$)) spectra were measured with a UR 70 (Zeiss, Jena) in KBr and M-40 (Zeiss, Jena) in methanol ($c = 4 . 10^{-5}$–10^{-4} mol dm^{-3}) spectrophotometers, respectively. The mass spectra (*m*/*z*; relative intensity, %) were run with an AEI MS 902 S apparatus at 70 eV. The NMR spectra (δ, ppm) were recorded with a Bruker AM 400 instrument operating at 400·13 MHz in tetramethylsilane containing hexadeuteriodimethyl sulfoxide solutions at 297 K, digital resolution 0·2 Hz per point for ^1H and 100·62 MHz, digital resolution 1·0 Hz per point for ^{13}C nuclei. The structure of compounds under study was evidenced and the signal positions were assigned employing the homonuclear decoupling[14] for ^1H NMR, and APT (ref.[15]), long-range INEPT (ref.[13]) and heterocorrelated 2D NMR (ref.[16]) for the ^{13}C NMR spectra.

2-Amino-5-ethoxycarbonyl-4-(2-furyl)-6-chloromethyl-3-cyano-4*H*-pyran (*I*)

Three drops of morpholine were added to a solution of ethyl 4-chloro-3-oxobutanoate (1·65 g) and 2-furylidenepropanedinitrile (1·44 g) in absolute ethanol (20 ml). The mixture was stirred for 6 h; already after 15 min colourless crystals began to separate. The product was filtered off, washed with a small amount of cool ethanol and crystallized from the same solvent. Yield 1·5 g (48%), m.p. 182–184°C. For $C_{14}H_{13}ClN_2O_4$ (308·7) calculated: 54·46% C, 4·25% H, 9·08% N, 11·48% Cl; found: 54·29% C, 4·27% H, 9·20% N, 11·59% Cl. UV spectrum: 230 (3·42), 286 sh (2·44). IR spectrum: 3 396 s, 3 323 s, 3 259 w, 3 216 m (NH_2), 3 193 m, 2 196 s (CN), 1 697 s (CO), 1 647 m, 1 606 m, 1 502 w, 1 470 w, 1 416 m (4*H*-pyran skeleton and C=C arom).

2-Ethoxymethylenamino-5-ethoxycarbonyl-4-(2-furyl)-6-chloromethyl-3-cyano-4*H*-pyran (*II*)

Suspension of 2-amino-4*H*-pyran *I* (1·0 g) in triethoxymethane (5 ml) was heated at 160°C for 16 h. The unreacted triethoxymethane was removed under diminished pressure and the residue was triturated with cool etanol (2 ml). The separated precipitate was filtered off and crystallized from ethanol. Yield 0·86 g (73%), m.p. 72–73°C. For $C_{17}H_{17}ClN_2O_5$ (364·8) calculated:

TABLE IV

^{13}C NMR chemical shifts of compounds *I*— *VI*

Compound	C-2	C-3	C-4	C-5	C-6	C-2β	C-3α	C-6α	C-5α	C-5β	C-5γ	Others
I	159·53	53·88	32·64	108·44	154·22	—	119·08	39·58	164·02	61·06	13·64	—
II	159·97	78·18	33·84	107·27	154·82	162·15	116·52	39·52	163·70	61·16	13·61	[a]
III	159·75	69·97	33·87	107·27	154·27	155·09	118·66	39·70	164·06	60·96	13·92	—
	C-8a	C-4a	C-5	C-6	C-7	C-2	C-4	C-7α	C-6α	C-6β	C-6γ	Others
IV	161·46	92·55	29·91	108·46	155·92	156·74	162·27	39·99	164·29	60·99	13·77	—
V	161·61	92·99	29·92	106·62	159·83	156·50	162·24	42·90	165·30	60·55	13·91	[b]
	C-9a	C-4a	C-5	C-5a	C-8a	C-2	C-4	C-8	C-6	—	—	Others
VIb	161·92	93·26	26·67	107·84	161·66	156·62	163·41	47·85	166·29	—	—	[c]
VI	162·03	93·31	26·82	107·18	161·74	156·46	163·41	47·40	167·62	—	—	[d]
VId	162·10	93·36	26·82	107·34	161·41	156·46	163·44	47·82	167·37	—	—	[e]

[a] 64·27 (C-2γ), 13·72 (C-2δ or C-5γ); [b] *p*-tolyl: 145·89 (C-1), 112·45 (C-2), 129·20 (C-3), 124·26 (C-4), 19·96 (C-5); [c] *p*-tolyl: 136·54 (C-1), 118·32 (C-2), 129·15 (C-3), 132·21 (C-4), 20·22 (C-5), [d] 44·64 (C-7α), phenyl: 137·58 (C-1), 127·35 (C-2), 128·52 (C-3), 127·12 (C-4); [e] 44·64(C-7α), 29·96 (C-7β), 19·36 (C-7γ), 13·47 (C-7δ).

55·97% C, 4·71% H, 7·68% N, 9·72% Cl; found: 55·65% C, 4·68% H, 7·89% N, 10·18% Cl. UV spectrum: 234 (3·34), 291 sh (2·78). IR spectrum: 3 139 w, 3 052 w, 2 978 m, 2 933 w, 2 215 m (CN), 1 723 s (CO), 1 683 m, 1 609 s, 1 508 w, 1 471 w, 1 436 w, 1 384 w, 1 369 w (4*H*-pyran skeleton and C=C arom).

5-Ethoxycarbonyl-2-formamidino-4-(2-furyl)-6-chloromethyl-3-cyano-4*H*-pyran (*III*)

Aqueous ammonia (26%, 0·5 ml) was added to a stirred solution of 2-ethoxymethylenamino-4*H*-pyran *II* (1·15 g) in ethanol (10 ml). The mixture was stirred for 4 h, the separated precipitate was filtered off, washed with ethanol and crystallized from ethanol. Yield 0·65 g (61%), m.p. 180–181°C. For $C_{15}H_{14}ClN_3O_4$ (335·8) calculated: 53·65% C, 4·21% H, 12·52% N, 10·56% Cl; found: 53·60% C, 4·34% H, 12·73% N, 10·74% Cl. UV spectrum: 208 (3·05), 257 (3·25), 305 (2·81). IR spectrum: 3 402 s (NH_2), 3 121 m, 2 978 w, 2 194 s (CN), 1 715 s (CO), 1 665 s, 1 617 s, 1 558 s, 1 496 w, 1 474 w, 1 432 w, 1 369 m (4*H*-pyran skeleton and C=C arom).

4-Amino-6-ethoxycarbonyl-5-(2-furyl)-7-chloromethyl-4*H*-pyrano[2,3-*d*]pyrimidine (*IV*)

Suspension of 4*H*-pyran *III* (5·0 g) in aqueous ethanol (50%, 50 ml) was refluxed for 8 h and then left to stand for 12 h. The separated precipitate was filtered off and crystallized from ethanol. Yield 3·5 g (70%), m.p. 101–103°C. For $C_{15}H_{14}ClN_3O_4$ (335·8) calculated: 53·65% C, 4·21% H, 12·52% N, 10·56% Cl; found: 53·64% C, 4·30% H, 12·61% N, 10·52% Cl. UV spectrum: 211 (3·35), 243 (3·10). IR spectrum: 3 459 m, 3 377 m, 3 319 m (NH_2), 3 202 m, 3 119 m, 2 980 w, 1 706 s (CO), 1 655 s, 1 603 s, 1 562 s, 1 502 w, 1 482 m, 1 436 s, 1 394 w, 1 372 w (C=C arom).

4-Amino-6-ethoxycarbonyl-5-(2-furyl)-7-*p*-toluidinomethyl-4*H*-pyrano[2,3-*d*]pyrimidine (*V*)

A mixture consisting of 2-formamidino-4*H*-pyran *III* (1·1 g), anhydrous potassium carbonate (0·46 g) and *p*-toluidine (0·71 g) in acetonitrile (30 ml) was stirred at room temperature for 16 h, and afterwards poured into water (300 ml). The yellow oil, which separated, solidified on standing. The solid was filtered off, washed with water and ether and purified by column chromatography on silica gel (chloroform). Yield 0·52 g (39%), m.p. 161–163°C (toluene). For $C_{22}H_{22}N_4O_4$ (406·5) calculated: 65·00% C, 5·47% H, 13·79% N; found: 65·15% C, 5·45% H, 14·00% N. UV spectrum: 220 (3·30) 243 (3·08). IR spectrum: 3 473 m, 3 400 m, 3 300 w (NH), 3 089 s, 2 965 w, 1 683 s (CO), 1 643 s, 1 556 s, 1 513 m, 1 469 m, 1 427 s, 1 367 m (C=C arom).

4-Amino-7-phenyl-5-(2-furyl)-5*H*,6*H*,8*H*-pyrrolo[3′,4′ : 5,6]-4*H*-pyrano[2,3-*d*]pyrimidin-6-one (*VIa*)

A suspension of 4*H*-pyrano[2,3-*d*]pyrimidine *IV* (0·56 g) and aniline (0·31 g) in ethanol (10 ml) was refluxed for 20 h. The mixture was cooled, the white crystals were filtered off, washed with ethanol and crystallized from dimethyl sulfoxide. Yield 0·30 g (52%), m.p. > 360°C. For $C_{19}H_{14}N_4O_3$ (346·4) calculated: 65·88% C, 4·08% H, 16·18% N; found: 65·81% C, 4·10% H, 16·05% N. UV spectrum (saturated solution): 200, 227, 267. IR spectrum: 3 364 m, 3 327 m, 3 140 s, 1 708 m, 1 683 s, 1 655 s, 1 580 s, 1 560 s, 1 480 s, 1 377 s.

4-Amino-5-(2-furyl)-7-*p*-tolyl-5*H*,6*H*,8*H*-pyrrolo-[3′,4′ : 5,6]-4*H*-pyrano[2,3-*d*]pyrimidin-6-one (*VIb*)

A) The tricyclic derivative *VIb* was synthesized from *IV* and *p*-toluidine by an analogous procedure as detailed for *VIa*. Yield 58%, m.p. > 360°C (dimethyl sulfoxide). For $C_{20}H_{16}N_4O_3$

(360·4) calculated: 66·65% C, 4·48% H, 15·55% N; found: 66·15% C, 4·44% H, 15·19% N. UV spectrum (saturated solution): 200, 259, 275. IR spectrum: 3 359 m, 3 320 m, 3 153 s, 1 703 m, 1 669 s, 1 647 s, 1 577 s, 1 553 s, 1 501 m, 1 480 m, 1 440 m, 1 427 m, 1 393 s.

B) Compound *V* (0·6 g), dissolved in dimethylformamide (10 ml), was refluxed for 2 h; after 10 min the solution began to be turbid with subsequent separation of crystals, which were separated and recrystallized from dimethyl sulfoxide. Yield 0·35 g (66%), m.p. >360°C. Spectral data of *VIb* were identical with those of the product prepared according to procedure *A*.

4-Amino-7-benzyl-5-(2-furyl)-5*H*,6*H*,8*H*-pyrrolo-
-[3′,4 : 5,6]-4*H*-pyrano[2,3-*d*]pyrimidin-6-one (*VIc*)

This compound was obtained from *IV* and benzylamine as described for the phenyl derivative *VIa*. Yield 60%, m.p. 265—267°C (dimethyl sulfoxide–water). For $C_{20}H_{16}N_4O_3$ (360·4) calculated: 66·64% C, 4·48% H, 15·55% N; found: 66·59% C, 4·51% H, 15·63% N. UV spectrum: 210 (3·43), 234 (3·24), 258 sh (3·02). IR spectrum: 3 327 m, 3 161 m, 2 908 w, 1 700 s, 1 675 s, 1 653 s, 1 583 s, 1 552 s, 1 483 m, 1 440 m, 1 427 m, 1 387 s.

4-Amino-7-butyl-5-(2-furyl)-5*H*,6*H*,8*H*-pyrrolo-
[3′,4 : 5,6]-4*H*-pyrano[2,3-*d*]pyrimidin-6-one (*VId*)

The title product was prepared from *IV* and butylamine by a similar procedure as *VIa*. Yield 46%, m.p. 233—235°C (ethanol). For $C_{17}H_{18}N_4O_3$ (326·4) calculated: 62·55% C, 5·57% H, 17·17% N; found: 62·30% C, 5·51% H, 17·05% N. UV spectrum: 214 (3·25), 234 (3·19), 256 sh (2·94). IR spectrum: 3 413 m, 3 300 w, 2 940 m, 2 913 m, 2 853 w, 1 699 s, 1 672 s, 1 636 s, 1 560 s, 1 480 w, 1 447 m, 1 427 m, 1 385 s.

Mass Spectra of Compounds *I*—*IV* and *VIb*

I: 310 (6), 308 (M^+, 19), 273 (19), 272 (50), 263 (7), 243 (8), 236 (9), 227 (7), 213 (8), 200 (38), 199 (12), 193 (25), 185 (10), 179 (6), 172/171 (12/9), 166/165 (5/7), 164 (12), 159/158 (8/6), 149 (10), 145/144 (14/91), 121/120 (22/7), 119/118 (28/7), 117/116 (19/28), 115 (100), 101 (6), 93/92 (10/6), 90/89 (7/25), 88/87 (12/28), 79 (7), 77/76 (25/6), 69 (12), 66/65 (33/22), 64/63 (13/19), 62 (13), 51/50 (11/7).

II: 366 (2), 364 (M^+, 8), 330 (4), 329/328 (10/27), 292/291 (3/3), 257/256 (5/7), 213 (7), 200 (6), 103 (12), 81 (4), 75/74 (9/7), 72 (5), 46/45 (44/83), 31 (100).

III and *IV*: 335 (M^+, 3), 306 (3), 292 (3), 290 (8), 286 (9), 273/272 (4/13), 271/270 (13/6), 264 (3), 262 (8), 258 (4), 256 (3), 255/254 (5/6), 243/242 (6/6), 228/227 (13/32), 226 (13), 214 (5), 200/199 (4/8), 198 (10), 172/171 (8/6), 149 (3), 146 (6), 144 (4), 116 (3), 89 (3), 77 (3), 63 (5), 46/45 (16/73).

VIb: 360 (M^+, 100), 361 (26), 332/331 (5/13), 227 (12), 199/198 (14/9), 186 (5), 171 (5), 149 (19), 120 (6), 118 (11), 111 (7), 109 (6), 107 (6), 97 (10), 95 (8), 91 (24), 85 (8), 83 (10), 81 (9), 79/78 (6/66), 77 (6), 71 (13), 70 (5), 69 (12), 67 (7), 65 (11), 63 (83), 57 (27), 54 (7).

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