Synthesis of 3-Amino-5*H*-1,2,3-triazino[5,4-*b*]indol-4-one. New Compounds with Blood Platelet Antiaggregation Activity.

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Starting with 3-aminoindole-2-carbohydrazide **1** a series of arylidene hydrazones **2** was obtained with good yields (79-85%). Upon treating **2** with nitrous acid a series of 3-arylidineamino-5*H*-1,2,3-triazino[5,4-*b*]indol-4-ones **3** was obtained (80-86%). The reaction of 4-methoxybenzylidene derivative **3e** with hydrazine hydrate, in ethanol, gave 3-amino-5*H*-1,2,3-triazino[5,4-*b*]indol-4-one **4** (64%). However, by treating **3e** in boiling hydrate, 3-aminoindole-2-carbaldehyde azine **5** was obtained (44%). By boiling **1** in *N*,*N*-dimethylformamide, 3-amino-5*H*-pyrimido[5,4-*b*]indol-4-one, **6** was obtained (52%).

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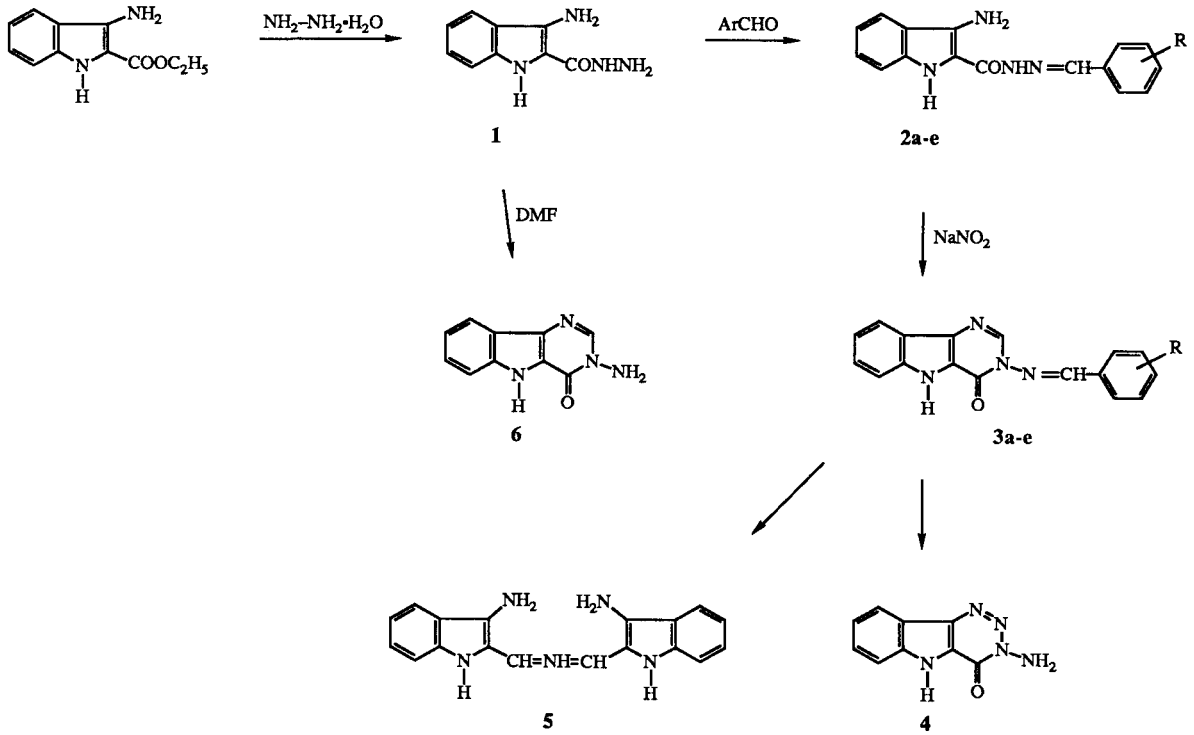
During the last few years, special attention has been focused on the synthesis of 1,2,3-triazin-4-ones fused with different carbocyclic and heterocyclic systems such as benzene [1-3], imidazole [4], indole [5] and pyridine [6], due to their importance within the pharmacological field of study. These compounds are generally obtained by diazotization and further cyclization of 2-aminoaryl (or heteroaryl) carbohydrazides [6] and also by intramolecular cyclization of aryl (or heteroaryl) triazenes with ortho acyl, cyano or alkoxycarbonyl substituents [5].

In the last few years we have reported [7-9] the synthesis of several fused systems of indole and different nitrogenous heterocyclic compounds, such as 1,2,4-triazino[5,6-*b*]indoles [7], 1,2,3-triazino[5,4-*b*]indoles [8] and 1,2,4-triazino[4,5-*a*]indoles [9]. In this paper we are reporting the synthesis of 3-amino-5*H*-1,2,3-triazino[5,4-*b*]indol-4-one (**4**, see Scheme) along with some related compounds, and in addition a new synthesis of 3-amino-5*H*-pyrimido-[5,4-*b*]indol-4-one (**6**), a compound which was previously reported by us [10].

Scheme I



The compounds were obtained as illustrated in the scheme, starting with 3-aminoindole-2-carbohydrazide **1** [10]. The preparation of this compound has been slightly modified. Compound **1** reacted with equimolecular amounts of several aromatic aldehydes in boiling ethanol to give hydrazones **2**, with goods yields (79-85%). Treating **2** with sodium nitrite, in aqueous hydrochloric acid, yielded 3-arylideneamino triazinones **3** (80-86%). Two different sequences are possible for this reaction: a) diazotization of the 3-amino group or b) *N*-nitrosation of the -CONH- group, and subsequent cyclization in both cases. We cannot decide between both possibilities. The hydrazinolysis of the 4-methoxybenzylidene group in **3e** carried out with hydrazine hydrate in ethanol gave 3-amino-5*H*-1,2,3-triazino[5,4-*b*]indol-4-one **4** (64%).

On the other hand, when **3e** was boiled with hydrazine hydrate for 5 hours a more complex reaction took place and the azine **5** (44%) was obtained. Compound **6** was obtained (52%) boiling **1** in *N*,*N*-dimethylformamide. This compound has been previously reported by us [11], treating **1** with ethyl orthoformate to give 3-ethoxymethylenamino-5*H*-pyrimido[5,4-*b*]indol-4-one and subsequent basic hydrolysis.

All the new compounds were characterized by elemental analysis CHN and ir and ^{1}H-nmr spectroscopic data. In addition, **5** was also characterized by ms and ^{13}C-nmr spectroscopies.

In preliminary experiments, compounds **2a-g**, **3a-g**, **4** and **6** have shown activity as inhibitors of platelet aggregation induced by adenosin-5'-diphosphate (ADP) or arachidonic acid (AA), according to the Cardinal and Flowers method [12], in guinea-pig whole blood. The compounds **2f**, **2g**, **3f** and **3g** stand out for their activity, with an inhibition of 100% of the aggregation induced by ADP (23 μM) and AA (500 μM). Further details about this activity and other cardiovascular properties of these compounds will be published shortly.

EXPERIMENTAL

Melting points were determined in a Kofler apparatus and are uncorrected. Elemental analyses were obtained from vacuum-dried samples (over phosphorous pentoxide at 3-4 mm Hg, 2-3 hours, at about 60-70°). Infrared spectra were recorded on a Perkin-Elmer 687 apparatus, using potassium bromide tablets; the frequencies were expressed in cm^{-1}. The ^{1}H-nmr spectra were obtained on a Brüker AC 200 E instrument, with tetramethylsilane as the internal reference, at a concentration of about 0.1 g/ml and with dimethyl sulfoxide-d_6 as the solvent; the chemical shifts are reported in ppm from tetramethylsilane and are given in δ units, and the abbreviations are the usual. The ^{13}C-nmr spectra were obtained on a Brüker AC 200 E instrument, with tetramethylsilane as the internal reference, at a concentration of about 0.2 g/ml and with dimethyl sulfoxide-d_6 as the solvent; the chemical shifts are reported in ppm from tetramethylsilane. The mass spectra (ms) were recorded in a Hewlett-Packard 5988 A apparatus by direct insertion probe (DIP) and electronic ionization. Thin-layer chromatography (tlc) was carried out in silica gel (DSF-5, Cammaga, 0.3 mm thickness) with TDA (toluene, dioxane, acetic acid; 90:25:4)) as the solvent and the plates were scanned under ultraviolet light, λ = 254 and 366 nm. Solvents were usually removed in vacuum, using a rotatory evaporator, when stated.

3-Aminoindole-2-carbohydrazide (**1**).

This compound was obtained after making a slight modification of a reported method [10]. A suspension of ethyl 3-aminoindole-2-carboxylate (2.05 g, 10 mmoles) [11,13] and hydrazine hydrate (25 ml) was boiled for 4 hours. The cooled mixture was poured on ice (200 g) and the solid material was collected, washed with water and recrystallized, mp 165° (ethanol/water), pale brown needles, yield 1.50 g (79%).

N^2-Arylidene Hydrazones of 3-Aminoindole-2-carbohydrazide (**2**).

General Procedure.

The respective aromatic aldehyde (2.4 mmoles) was added to a solution of **1** (0.50 g, 2.6 mmoles) in ethanol (20 ml). The mixture was boiled for 10 minutes and cooled. The solid material was collected, washed with ethanol/water (1:1, 3 x 25 ml) and recrystallized as indicated. In this way, the following compounds were obtained:

2-(4-Phenylbenzylidene)-1-(3-aminoindole)-2-carbohydrazine **2a**.

From 4-biphenylcarbaldehyde (0.44 g, 2.4 mmoles), **2a** had mp 222-223° (from dioxane), yield 0.71 g (84%), as yellow coloured crystals; ir: 3400 (NH), 1650 (C=O), 1600 (C=N), 830 (aromatic 1,4-disubst), 730 (aromatic 1,2-disubst), 690 (aromatic monosubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 5.93 (bs, 2H, NH_2, deuterium oxide-exchangeable), 6.92 (m, 1H, H-5), 7.22 (m, 1H, H-6), 7.32-7.49 (m, 3H, arom), 7.70-7.85 (m, 8H, arom), 8.24 (s, 1H, CH=N), 10.11 (s, 1H, NH-indole, deuterium oxide-exchangeable), 11.00-11.40 (bs, 1H, NH-CO, deuterium oxide-exchangeable).

Anal. Calcd. for $C_{22}H_{18}H_4O$: C, 74.57; H, 5.08; N, 15.84. Found: C, 74.37; H, 5.14; N, 15.84.

2-(4-Nitrobenzylidene)-1-(3-aminoindole)-2-carbohydrazine **2b**.

From 4-nitrobenzaldehyde (0.36 g, 2.4 mmoles), **2b** had mp 294° (from dioxane), yield 0.66 g (85%), as garnet coloured needles; ir: 3420, 3360 (NH), 1630 (C=O), 1600 (C=N), 1500 (N=O), 1320 (N=O), 730 (aromatic 1,2-disubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 5.80-6.20 (bs, 2H, NH_2, deuterium oxide-exchangeable), 6.95 (m, 1H, H-5), 7.25 (m, 1H, H-6), 7.34 (c, 1H, H-7), 7.78 (c, 1H, H-4), 8.02 (d, 2H, H-2' + H-6'), 8.30 (d, 2H, H-3' + H-5'), 8.29 (s, 1H, CH=N), 10.12 (s, 1H, NH-indole, deuterium oxide-exchangeable), 11.00-11.50 (bs, 1H, NH-CO, deuterium oxide-exchangeable).

Anal. Calcd. for $C_{16}H_{13}N_5O_3$: C, 59.44; H, 4.02; N, 21.67. Found: C, 59.46; H, 4.00; N, 21.56.

2-Benzylidene-1-(3-aminoindole)-2-carbohydrazine **2c**.

From benzaldehyde (0.25 g, 2.4 mmoles), **2c** had mp 190-191° (from ethanol), yield 0.53 g (80%), as greenish-yellow coloured crystals; ir: 3480, 3420, 3380 (NH), 1640 (C=O), 1600 (C=N), 740 (aromatic 1,2-disubst), 690 (aromatic monosubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 5.60-6.00 (bs, 2H, NH_2, deuterium oxide-exchangeable) 6.77 (m, 1H, H-5), 7.07 (m, 1H, H-6), 7.25-7.35 (m, 3H, arom), 7.50-7.60 (m, 3H, arom), 8.05 (s, 1H, CH=N), 9.95 (s, 1H, NH-indole, deuterium oxide-exchangeable), 10.90-11.40 (bs,

1H, NH-CO, deuterium oxide-exchangeable).

Anal. Calcd. for $C_{16}H_{14}N_4O$: C, 69.06; H, 5.03; N, 20.14. Found: C, 69.22; H, 5.22; N, 20.37.

2-(4-Chlorobenzylidene)-1-(3-aminoindole)-2-carbohydrazine **2d**.

From 4-chlorobenzaldehyde (0.34 g, 2.4 mmoles), **2d** had mp 225° (from ethyl acetate/ethanol), yield 0.60 g (79%), as yellow coloured crystals; ir: 3440, 3270 (NH), 1615 (C=O), 1570 (C=N), 735 (aromatic 1,2-disubst.) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 5.80-6.20 (bs, 2H, NH_2, deuterium oxide-exchangeable) 6.94 (m, 1H, H-5), 7.24 (m, 1H, H-6), 7.35 (m, 1H, H-7), 7.53 (d, 2H, H-3′+H-5′), 7.65-7.80 (m, 3H, H-4+H-2′+H-6′), 8.22 (s, 1H, CH=N), 10.92 (s, 1H, NH-indole, deuterium oxide-exchangeable), 11.00-11.50 (bs, 1H, NH-CO, deuterium oxide-exchangeable).

Anal. Calcd. for $C_{16}H_{13}ClN_4O$: C, 61.44; H 4.16; N, 17.92. Found: C, 61.20; H, 4.26; N, 17.77.

2-(4-Methoxybenzilidene)-1-(3-aminoindole)-2-carbohydrazine **2e**.

From 4-methoxybenzaldehyde (0.32 g, 2.4 mmoles), **2e** had mp 185° (from ethyl acetate), yield 0.60 g (80%), as yellow coloured needles; ir: 3480, 3380, 3260 (NH), 1610 (C=O), 1560 (C=N), 1250 (C-O), 820 (aromatic 1,4-disubst), 730 (aromatic 1,2-disubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 3.66 (s, 3H, CH_3O), 5.65-5.85 (bs, 2H, NH_2, deuterium oxide-exchangeable), 6.79 (m, 1H, H-5), 6.87 (d, 2H, H-3′ + H-5′), 7.08 (m, 1H, H-6), 7.20 (m, 1H, H-7), 7.53-7.62 (m, 3H, H-4 + H-2′ + H-6′), 8.02 (s, 1H, CH-N), 9.96 (s, 1H, NH-indole deuterium oxide-exchangeable), 10.70-11.00 (bs, 1H, NH-CO, deuterium oxide-exchangeable).

Anal. Calcd. for $C_{17}H_{16}N_4O_2$: C, 66.23; H, 5.19; N, 18.18. Found: C, 66.52; H, 5.35; N, 18.07.

2-(3,4,5-Trimethoxybenzylidene)-1-(3-aminoindole)-2-carbohydrazine **2f**.

From 3,4,5-trimethoxybenzaldehyde (0.47 g, 2.40 mmoles), **2f** had mp 191-192° (from dioxane), yield 0.72 g (85%), as yellow coloured spongy crystals; ir: 3420, 3360, 3280 (NH), 1610 (C=O), 1575 (C=N), 1325 (C-O), 740 (aromatic 1,2-disubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 3.72 (s, 3H, CH_3), 3.87 (s, 6H, CH_3), 5.70-6.20 (bs, 2H, NH_2, deuterium oxide-exchangeable), 6.94 (t, 1H, H-5), 7.07 (s, 2H, H-2′ + H-6′), 7.24 (t, 1H, H-6), 7.31 (d, 1H, H-7), 7.77 (d, 1H, H-4), 8.15 (s, 1H, CH=N), 10.14 (s, 1H, NH indole, deuterium oxide-exchangeable), 10.80-11.30 (bs, 1H, NHCO, deuterium oxide-exchangeable).

Anal. Calcd. for $C_{18}H_{17}N_5O_2$: C, 64.47; H, 5.07; N, 20.89. Found: C, 64.57; H, 5.31; N, 20.80.

2-(4-Acetamidobenzyliden)-1-(3-aminoindole)-2-carbohydrazide **2g**.

From 4-acetamidobenzaldehyde (0.39 g, 2.4 mmoles), **2g** had mp 238° (from dioxane), yield 0.63 g (78%) as yellow coloured needles; ir: 3440, 3280 (NH), 1650 (C=O), 1620 (C=O), 1600 (C=N), 740 (aromatic 1,2-disubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 2.07 (s, 3H, CH_3), 5.60-6.30 (bs, 2H, NH_2, deuterium oxide-exchangeable), 6.94 (t, 1H, H-5), 7.23 (t, 1H, H-6), 7.34 (d, 1H, H-7), 7.69 (s, 4H, H-2′ + H-3′ + H-5′ + H-6′), 7.76 (d, 1H, H-4), 8.16 (s, 1H, CH=N), 10.11 (s, 1H, $NHCOCH_3$, deuterium oxide-exchangeable), 10.14 (s, 1H, NH indole, deuterium oxide-exchangeable).

Anal. Calcd. for $C_{19}H_{20}N_4O_4$: C, 61.95; H, 5.43; N, 15.22. Found: C, 62.10; H, 5.62; N, 14.95.

3-Arylidenamino-5*H*-1,2,3-triazino[5,4-*b*]indol-4-ones (**3**).

General Procedure.

Concentrated hydrochloric acid (0.5 ml) and then a 20% (w/v) aqueous solution of sodium nitrite (5 ml) were added to a stirred suspension of the respective compounds **2** (0.5 g) in water (25 ml). The mixture was stirred at room temperature for 15 hours. The solid material was collected, washed with warm water and recrystallized as indicated. In this way, the following compounds were obtained:

3-(4-Phenylbenzylideneamino)-5*H*-1,2,3-triazino[5,4-*b*]indol-4-one **3a**.

From **2a** (0.5 g, 1.41 mmoles), **3a** had mp 246-247° (from ethanol/*N*,*N*-dimethylformamide), yield 0.41 g (80%), as yellow coloured crystals; ir: 3130 (NH), 1680 (C=O), 1595 (C=N), 740 (aromatic 1,2-disubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 7.40-7.60 (m, 4H, arom), 7.65-7.75 (m, 2H, arom), 7.81 (d, 2H, arom), 7.92 (d, 2H, arom), 8.16 (d, 2H, arom), 8.26 (d, 1H, H-9), 9.36 (s, 1H, CH=N), 13.45 (s, 1H, NH-indole, deuterium oxide-exchangeable).

Anal. Calcd. for $C_{22}H_{15}N_5O$: C, 72.32; H, 4.11; N, 19.17. Found: C, 72.41; H, 4.30; N, 19.35.

3-(4-Nitrobenzylideneamino)-5*H*-1,2,3-triazino[5,4-*b*]indol-4-one **3b**.

From **2b** (0.55 g, 1.55 mmoles), **3b** had mp 243-244° (from *N*,*N*-dimethylformamide), yield 0.44 g (85%), as orange coloured crystals; ir: 3200 (NH), 1690 (C=O), 1520, 1345 (N=O), 845 (aromatic 1,4-disubst), 745 (aromatic 1,2-disubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 7.48 (m, 1H, H-8), 7.67 (d, 2H, H-2′ + H-6′), 8.26-8.45 (m, 5H, H-6 + H-7 + H-9 + H-3′ + H-5′), 9.54 (s, 1H, CH=N), 13.48 (s, 1H, NH-indole deuterium oxide-exchangeable).

Anal. Calcd. for $C_{16}H_{10}N_6O_3$: C, 57.48; H, 2.99; N, 25.15. Found: C, 57.35; H, 2.95; N, 25.02.

3-Benzylideneamino-5*H*-1,2,3-triazino[5,4-*b*]indol-4-one **3c**.

From **2c** (0.50 g, 1.8 mmoles), **3c** had mp 223-224° (from dioxane), yield 0.41 g (81%), as a brown coloured powder; ir: 3140 (NH), 1720 (C=O), 1605 (C=N), 740 (aromatic 1,2-disubst), 690 (aromatic monosubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 7.45 (m, 1H, H-8), 7.59-7.70 (m, 5H, C_6H_5-), 8.00-810 (m, 2H, H-6 + H-7), 8.24 (m, 1H, H-9), 9.30 (s, 1H, CH=N), 13.25-13.40 (bs, 1H, NH-indole deuterium oxide-exchangeable).

Anal. Calcd. for $C_{16}H_{11}N_5O$: C, 66.44; H, 3.80; N, 24.22. Found: C, 66.59; H, 4.02; N, 24.30.

3-(4-Chlorobenzylideneamino)-5*H*-1,2,3-triazino[5,4-*b*]indol-4-one **3d**.

From **2d** (0.50 g, 1.6 mmoles), **3d** had mp 247-248° (from *N*,*N*-dimethylformamide), yield 0.44 g (86%), as yellow coloured crystals; ir: 3130 (NH), 1690 (C=O), 1610 (C=N), 830 (aromatic 1,4-disubst), 740 (aromatic 1,2-disubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 7.44 (m, 1H, H-8), 7.56-7.72 (m, 4H, H-6 + H-7 + H-3′ + H-5′), 8.02 (d, 2H, H-2′ + H-6′), 8.23 (m, 1H, H-9), 9.32 (s, 1H, CH=N), 13.37 (s, 1H, NH-indole, deuterium oxide-exchangeable).

Anal. Calcd. for $C_{16}H_{10}ClN_5O$: C, 59.35; H, 3.09; N, 21.63. Found: C, 59.54; H, 3.14; N, 21.84.

3-(4-Methoxybenzylideneamino)-5*H*-1,2,3-triazino[5,4-*b*]indol-4-one **3e**.

From **2e** (0.5 g, 1.62 mmoles), **3e** had mp 190-191° (from ethanol/*N*,*N*-dimethylformamide), yield 0.43 g (83%), as a pale

yellow crystals; ir: 3140 (NH), 1695 (C=O), 1605 (C=N), 1260 (C-O), 835 (atomatic 1,4-disubst), 745 (aromatic 1,2-disubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 3.85 (s, 3H, CH_3O), 7.12 (d, 2H, H-3' + H-5'), 7.44 (m, 1H, H-8), 7.59-7.70 (m, 2H, H-6 + H-7), 7.98 (d, 2H, H-2' + H-6'), 8.22 (m, 1H, H-9), 9.15 (s, 1H, CH=N), 13.29 (s, 1H, NH-indole, deuterium oxide-exchangeable).

Anal. Calcd. for $C_{17}H_{13}N_5O_2$: C, 63.94; H, 4.07; N, 21.94. Found: C, 63.99; H, 4.13; N, 22.00.

3-(3,4,5-Trimethoxybenzylideneamino)-5*H*-1,2,3-triazino[5,4-*b*]indol-4-one, **3f**.

From **2f** (0.5 g, 1.38 mmoles), **3f** had mp 232-233° (from ethanol/*N*,*N*-dimethylformamide), yield 0.57 g (84%), as yellow solid; ir: 3140 (NH), 1695 (C=O), 1580 (C=N), 1130 (C-O), 740 (aromatic 1,2-disubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 3.81 (s, 3H, CH_3), 3.92 (s, 6H, CH_3), 7.43-7.53 (m, 3H, H-8 + H-2' + H-6'), 7.62-7.74 (m, 2H, H-7 + H-6), 8.30 (d, 1H, H-9), 9.23 (s, 1H, CH=N), 13.30-13.45 (bs, 1H, NH indole, deuterium oxide-exchangeable).

Anal. Calcd. for $C_{19}H_{17}N_5O_4$: C, 60.16; H, 4.48; N, 18.47. Found: C, 60.40; H, 4.63; N, 18.65.

3-(4-Acetamidobenzylideneamino)-5*H*-1,2,3-triazino[5,4-*b*]indol-4-one, **3g**.

From **2g** (0.5 g, 1.41 mmoles), **3g** had mp > 250° (from *N*,*N*-dimethylformamide), yield 0.43 g (84%) as yellow coloured spongy solid; ir: 3420, 3100 (NH), 1685 (C=O), 1610 (C=O), 825 (aromatic 1,4-disubst), 740 (aromatic 1,2-disubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 2.12 (s, 3H, CH_3), 7.49 (t, 1H, H_8), 7.60-7.72 (m, 2H, H-7 + H-6), 7.81 (d, 2H, H-3' + H-5'), 8.00 (d, 2H, H-2' + H-6'), 8.27 (d, 1H, H-9), 9.28 (s, 1H, CH=N), 10.33 (s, 1H, NHCO, deuterium oxide-exchangeable), 13.35 (s, 1H, NH indole, deuterium oxide-exchangeable).

Anal. Calcd. for $C_{18}H_{14}N_6O.H_2O$: C, 59.34; H, 4.39; N, 23.08. Found: C, 59.56; H, 4.51; N, 23.51.

3-Amino-5*H*-1,2,3-triazino[4,5-*b*]indol-4-one (**4**).

A mixture of **3e** (0.5 g, 1.56 mmoles), ethanol (25 ml) and hydrazine hydrate (3 ml) was boiled for 5 hours. The mixture was cooled and the solid material was collected, washed with water and then with ethanol and recrystallized, mp 225° (from ethanol/-*N*,*N*-dimethylformamide), yield 0.19 g (64%), as brown coloured needles; ir: 3360, 3190 (NH), 1700 (C=O), 750 (aromatic 1,2-disubst) cm^{-1}; ^{1}H-nmr (DMSO-d_6): δ 6.98 (s, 2H, NH_2), 7.43 (m, 1H, H-8), 7.52-7.65 (m, 2H, H-6 + H-7), 8.24 (m, 1H, H-9), 12.30-13.00 (bs, 1H, NH-indole, deuterium oxide-exchangeable).

Anal. Calcd. for $C_9H_7N_5O$: C, 53.73; H, 3.48; N, 34.82. Found: C, 53.98; H, 3.58; N, 35.02.

3-Aminoindole-2-carbaldehyde Azine (**5**).

A mixture of **3e** (0.5 g, 1.56 mmoles) and hydrazine hydrate (10 ml) was boiled for 5 hours. Solvents were removed in vacuum and the residual material dispersed in ethanol/water (1/1). The solid material was collected and recrystallized, mp 238-240° dec (from *N*,*N*-dimethylformamide/ethanol), yield 0.11 g (44%), as orange coloured powder; ir: 3410, 3200 (NH), 1600 (C=N), 745 (aromatic 1,2-disubst); ^{1}H-nmr (DMSO-d_6): δ 5.71 (bs, 2H, NH_2, deuterium oxide-exchangeable) 6.88 (m, 1H, H-5), 7.10-7.25 (m, 2H, H-6 + H-7), 7.66 (m, 1H, H-4), 8.75 (s, 1H, CH=N), 10.29 (s, 1H, NH-indole, deuterium oxide-exchangeable); ^{13}C-nmr, 110.3 (C-3), 113.6 (C-7), 116.2 (C-6), 118.4 (C-4 or C-5), 118.8 (C-4 or C-5), 123.4 (C-2), 131.3 (C-3a), 136.2 (C-7a), 148.2 (CH=N); ms: (70 eV, electron impact), m/z (abundance %), 316 (28, M^+), 285 (13), 159 (100), 131 (43), 104 (16), 57 (20).

Anal. Calcd. for $C_{18}H_{16}N_6.\frac{2}{3}H_2O$: C, 65.85; H, 5.33; N, 25.60. Found: C, 66.08; H, 5.05; N, 25.30.

3-Amino-5*H*-pyrimido[5,4-*b*]indol-4-one (**6**).

A mixture of **1** (0.5 g, 2.63 mmoles) and *N*,*N*-dimethylformamide (10 ml) was boiled for 10 hours. The solvent was removed and the residual material dispersed in ethanol. The solid material was collected and recrystallizated, mp 250° (from ethanol/*N*,*N*-dimethylformamide), yield 0.28 g (52%), as white crystals, reported [10], mp 250°.

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