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Dedicated to the memory of Professor Giuseppe Bellucci (1940-1996)

A new 4-(benzotriazol-1-yl)-1,2,3-triazole structure was obtained by the diazotization reaction of either of 1-(2-aminophenyl)-4-carboxamido-5-amino-1*H*-1,2,3-triazole (**1c**) or of the corresponding Dimroth isomer **1d**. It underwent some common reactions to evaluate its chemical behaviour and structure. An analogous reaction sequence was carried out from the 2-nitro-4-methylphenyl azide, to assign the structure to the nitro derivatives prepared. The structure of the new compounds prepared was confirmed by chemical and spectroscopic methods.

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A new 4-(benzotriazol-1-yl)-1,2,3-triazole structure **A** was obtained while pursuing our researches on derivatives of medicinal interest bearing the 1,2,3-triazole ring fused with a benzodiazepine [1] or a quinazoline [2] ring, in order to synthesize the new tricyclic 1,2,3-triazolo[1,5-*e*]-[1,2,3,5]benzotetrazepines **B** (Figure 1).

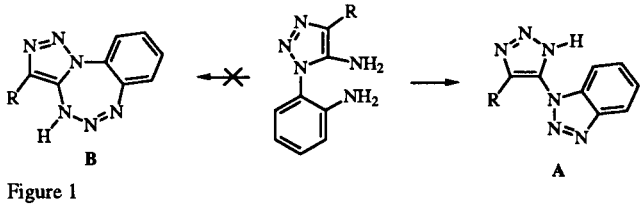


Figure 1

The new heterocycles then underwent some common chemical reactions to evaluate the acid-base properties and its behaviour towards electrophilic substitution, *N*-alkylation and oxidation, as well as to confirm its structure (see structure discussion).

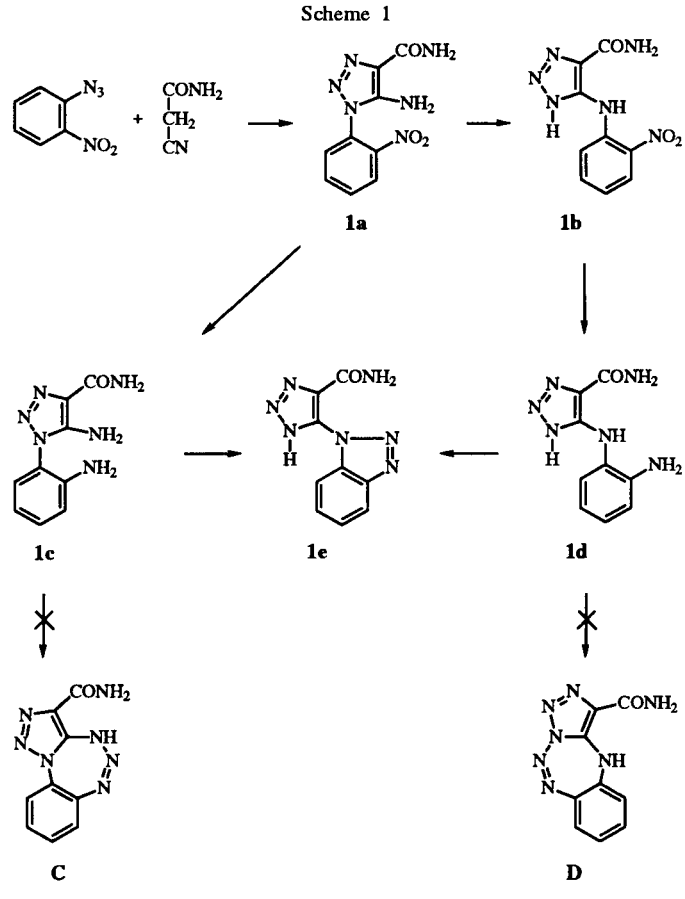
The ionic 1,3-dipolar cycloaddition reaction (Scheme 1) of *ortho*-nitrophenyl azide [3] to cyanacetamide at room temperature, gave the expected 1-(2-nitrophenyl)-4-carboxamido-5-amino-1*H*-1,2,3-triazole (**1a**) in good yield. This structure was also confirmed by obtaining the corresponding Dimroth isomer **1b**, by heating **1a** in boiling ethanol or from the mother liquors of the **1a** preparation. The nitrophenyl-1,2,3-triazoles **1a** and **1b** were then converted, by catalytic hydrogenation, into the aminophenyl derivative **1c** and the isomeric **1d** respectively.

Both compounds, by a diazotization reaction with nitrous acid in an aqueous acid solution, provided the same compound, the 4-(benzotriazol-1-yl)-5-carboxamido-1,2,3-triazole **1e**.

Clearly, the diazonium salt obtained from **1d** reacted by an intramolecular insertion to the amino function on the triazole ring, to give **1e**, which precipitated as a crystalline solid, in the same way as obtaining the benzotriazole from *ortho*-phenylendiamine [4], while for the intramolecular reaction of the diazonium salt **1c**, it is necessary to involve the equilibrium connected with Dimroth isomerization [5].

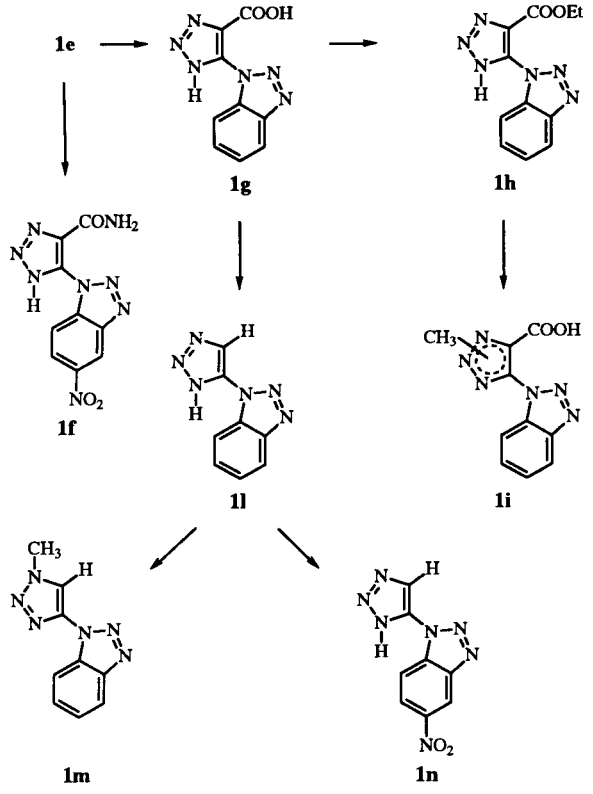
Compound **1e** (Scheme 2) in concentrated sulfuric acid reacted with potassium nitrate at 60° to give the mononitro derivative **1f** in 77% yield. Alkaline or acid hydrolysis of **1e** provided the corresponding carboxylic acid **1g** in

Scheme 1



good yield and this, by the usual Fisher procedure, was converted into the ethyl ester **1h**.

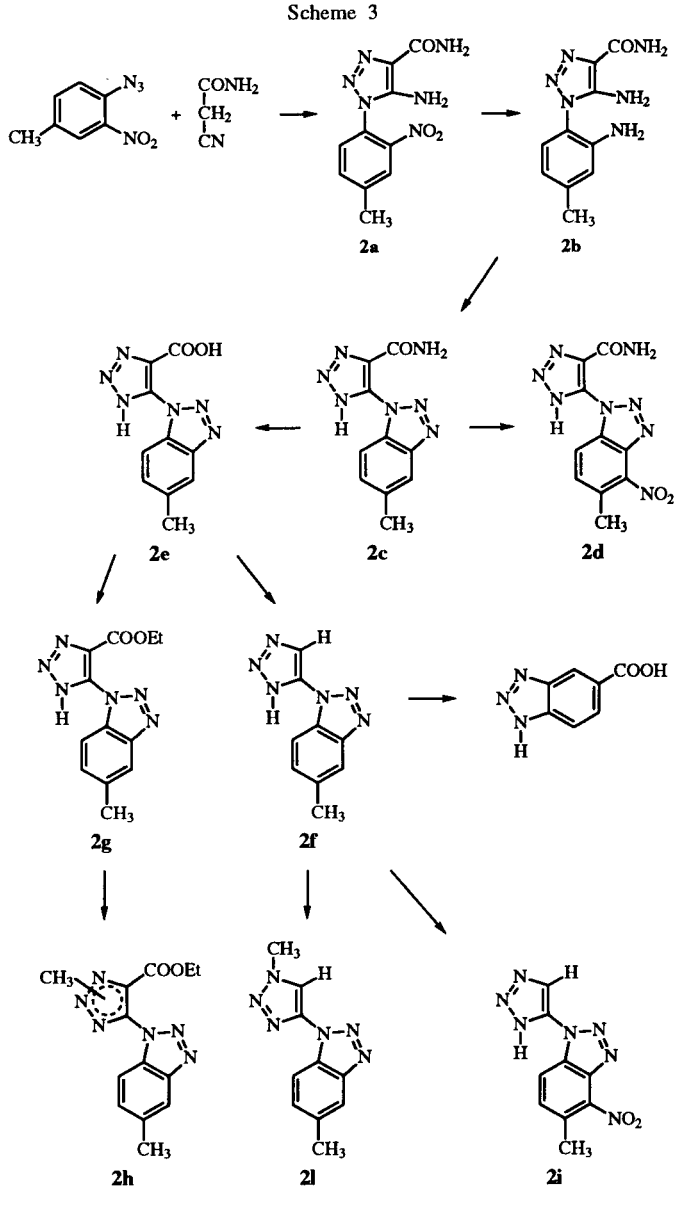
Scheme 2



This procedure represented the synthetic route to the ester derivative, because the 1,3-dipolar cycloaddition reaction of *ortho*-nitrophenylazide to ethyl cyanacetate failed, according to previous experiments [6]. Compound **1h** underwent an *N*-alkylation with dimethyl sulfate-potassium carbonate in anhydrous acetone to give a mixture of the acid *N*-methyl derivatives **1i** (1- and 2-methyl substituted isomers by ^{1}H-nmr analysis) which were not separated. The acid derivative **1g**, by refluxing in dimethylformamide, easily decarboxylated to the unsubstituted compound **1l**, which dissolved in 10% sodium carbonate. These acidic properties, associated with the 1,2,3-triazole conjugated with the benzotriazole ring, were also present in the amide **1e** and the ester **1h** derivatives (less soluble sodium salts precipitated in an excess of aqueous base). These acidic properties increased in the nitro derivatives. Compound **1l** was devoid of amphoteric properties because it was insoluble in 10% hydrochloric acid. *N*-Methylation of **1l** with iodomethane in methanolic sodium hydroxide solution gave the 1-*N*-methyl derivative **1m**, isolated in 80% yield. Furthermore 4-(benzotriazol-1-yl)-1,2,3-triazole **1l** underwent nitration; under mild experimental conditions the mononitro derivative **1n** was obtained in high yield, but under stronger nitration conditions a decomposition product, (5-nitrobenzotriazole) [7] was isolated rather than a polynitro compound.

A similar reaction sequence (Scheme 3) was carried out from 2-nitro-4-methylphenyl azide [8], to prepare analogous 4-(benzotriazol-1-yl)-1,2,3-triazoles, bearing a methyl substituent on a known phenyl ring position, which were useful for spectroscopic structure assignment for the nitro compounds. Under the experimental conditions described above, triazole derivatives **2a** and **2b** were prepared. It is worth noting that catalytic reduction of **2a** gave **2b** together with a by-product, isolated in small amount, and characterized as 4-methyl-*ortho*-phenylendiamine [9], probably coming from the **2b** Dimroth isomer present at the equilibrium. Treatment of **2b** with nitrous acid gave the expected

Scheme 3

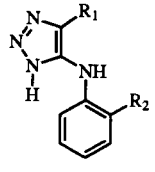


4-[5-(methyl)benzotriazol-1-yl]-5-carboxamido-1,2,3-triazole (**2c**) in good yield. This compound, similar to **1e**, was easily nitrated with potassium nitrate in sulfuric acid, to give the mononitro derivative **2d** which was easily hydrolyzed to the acid **2e**. Compound **2e** was decarboxylated to **2f**.

In contrast esterification of **2e** had to be carried out *via* an acyl chloride and ethanol. The ethyl ester **2g** was *N*-methylated with dimethyl sulfate-potassium carbonate in anhydrous acetone to give the expected mixture **2h** (1- and 2-*N*-methyl isomers by ^{1}H-nmr analysis) which was not separated.

Nitration of **2f** with concentrated nitric acid-sulfuric acid, provided the mononitro derivative **2i**, while the 1-*N*-methyl derivative **2l** was isolated by alkylation of **2f** with iodomethane in alkaline methanol. Finally **2f** underwent a side chain oxidation either in an acid (potassium dichromate) or an alkaline (potassium permanganate) medium: the only isolated product was the 5-carboxybenzotriazole [10]. The expected derivative 4-[(5-carboxy)benzotriazol-1-yl]-1,2,3-triazole was obtained in low yield together with the equally acidic starting material **2f** and identified in the mixture by spectroscopic data.

To assign the structure of *N*-methyl-1,2,3-triazole derivatives, the Dimroth isomers **1o-r** were also prepared (Figure 2). Compound **1o**, obtained from **1b** by alkaline hydrolysis, gave **1p** by reduction of the nitro group; compound **1q**, obtained from **1o** by decarboxylation, gave **1r** by reduction.



1o, R_1 = COOH; R_2 = NO_2
1p, R_1 = COOH; R_2 = NH_2
1q, R_1 = H; R_2 = NO_2
1r, R_1 = H; R_2 = NH_2

Figure 2

The structure determination of the new 4-(benzotriazol-1-yl)1,2,3-triazole derivatives required an accurate spectroscopic analysis and chemical evaluations.

In fact ^{1}H-nmr data showed remarkable disagreement with the 1,2,3-triazolo[1,5-*e*][1,2,3,5]benzotetraazepine C structure hypothesized from **1c** under those experimental conditions; at the same time, the analogous reaction carried out on the Dimroth isomer **1d** provided an identical compound **1e**, rather than the expected 1,2,3-triazolo-[1,5-*d*][1,2,3,5]benzotetraazepine isomer **D** (Scheme 1). In this case, however, the structural pattern corresponding to *o*-phenylendiamine, suggested the formation of a benzotriazole ring [4] and the resulting 4-(benzotriazol-1-yl)-1,2,3-triazole derivative **1e** agreed with the spectroscopic data (Tables I and II). This structural assignment could also be supported by the following chemical considerations:

a) Formation of the Dimroth isomer **1b** in the preparation of **1a** carried out at room temperature (procedure B) and the presence of the Dimroth equilibrium [5], as confirmed by obtaining a small amount of 4-methyl-*o*-phenylendiamine [9] from the catalytic hydrogenation of **2a** to give **2b**.

b) Isolation of substituted benzotriazoles from reactions which lead to structure decomposition. Thus nitration of **1l** under vigorous experimental conditions provided the 5-nitrobenzotriazole [7], clearly coming from the decomposition of the nitro derivative **1n**. Side chain oxidation of **2f**, by alkaline potassium permanganate or acid potassium dichromate, provided the 5-carboxybenzotriazole [10], clearly coming from the decomposition of the oxidation product 4-[5-(carboxy)benzotriazol-1-yl]-1,2,3-triazole, established in the reaction mixtures by spectroscopic means.

In the ^{1}H-nmr spectra of the 5-unsubstituted triazole compounds **1l-n** and **2f,i,l** the H-7' proton of the benzotriazole ring resonated 0.4 ppm further downfield than the 5-substituted triazoles (Table I). This relevant effect made the initially hypothesized benzotetraazepine structure **B**

Table I

^{1}H-NMR Data (δ, ppm) for some Compounds **1** and **2**

	5-H	4'-H	5'-H	6'-H	7'-H	CH_3	$J_{4'5'}$	$J_{4'6'}$	$J_{4'7'}$	$J_{5'6'}$	$J_{5'7'}$	$J_{6'7'}$	Other
1e	—	8.19	7.52	7.64	7.68	—	8.39	0.92	0.90	6.92	1.00	8.38	
1f	—	9.14	—	8.45	7.89	—	—	2.09	0.50	—	—	9.13	
1g	—	8.20	7.52	7.64	7.68	—	8.37	0.95	0.91	7.07	0.95	8.43	
1h	—	8.20	7.53	7.65	7.68	—	8.34	0.93	0.85	7.07	1.07	8.26	4.12, 0.93, J 7.10
1l	8.56	8.15	7.51	7.68	8.09	—	8.40	0.99	0.95	7.03	1.00	8.41	
1m	8.80	8.17	7.52	7.69	8.10	—	8.32	1.12	0.88	6.98	1.10	8.32	4.23
1n	8.63	9.07	—	8.48	8.27	—	—	2.08	0.50	—	—	9.14	
2c	—	7.94	—	7.45	7.57	2.49	—	1.44	0.50	—	—	8.57	
2d	—	—	—	7.67	7.88	2.57	—	—	—	—	—	8.61	
2e	—	7.94	—	7.46	7.53	2.51	—	1.62	0.52	—	—	8.52	
2f	8.52	7.90	—	7.49	7.97	2.48	—	1.47	0.50	—	—	8.54	
2g	—	7.96	—	7.47	7.56	2.51	—	1.39	0.50	—	—	8.55	4.14, 0.96, J 7.09
2i	8.63	—	—	7.74	8.26	2.58	—	—	—	—	—	8.65	
2l	8.79	7.94	—	7.53	7.99	2.49	—	1.53	0.65	—	—	8.53	4.21

Table II

^{13}C NMR Data (δ, ppm) for some Compounds **1** and **2**

	4-C	5-C	3a'-C	4'-C	5'-C	6'-C	7'-C	7'a-C	C=O	CH_3	Other
1e	139.1	133.3	144.2	118.8	124.1	128.2	110.6	132.8	159.2	—	
1f	139.2	134.5	144.9	116.9	144.0	123.8	112.7	136.4	159.8	—	
1g	140.3	130.3	144.1	118.8	124.1	128.2	110.2	133.1	158.8	—	
1h	140.9	130.9	144.6	119.3	124.6	128.8	110.7	133.6	158.1	—	61.0, 13.2
1l	142.2	121.1	144.6	118.9	124.4	128.4	111.0	130.9	—	—	
1m	142.2	118.1	145.0	119.4	124.8	128.9	111.4	131.5	—	—	37.1
1n	142.0	122.0	144.9	116.6	144.2	123.7	112.8	133.9	—	—	
2c	139.7	133.5	145.3	118.1	134.4	130.6	110.7	131.8	158.7	20.7	
2d	138.3	134.2	139.0	137.5	128.8	132.5	115.4	133.7	159.6	17.3	
2e	140.8	n.d.	145.2	118.1	134.3	130.6	110.3	132.1	159.3	20.6	
2f	142.4	121.4	145.7	118.2	134.6	130.8	111.0	129.8	—	20.6	
2g	141.0	n.d.	145.2	118.1	134.4	130.7	110.2	132.0	158.2	20.6	61.0, 13.2
2i	141.9	121.8	138.3	137.8	128.8	132.8	115.6	131.6	—	17.2	
2l	142.3	118.0	145.6	118.2	134.6	130.9	111.0	130.0	—	20.7	37.1

doubtful, in which H-7' proton and the substitution site were so distant, while it was explainable for the triazole-benzotriazole structure **A**, assuming an easily predictable and different rotameric equilibrium around the N-1'-C-4 bond between unsubstituted and substituted compounds.

Moreover, in the ^{13}C-nmr spectra (Table II), the benzene ring resonances of all the compounds strictly corresponded with those described for the benzotriazole derivatives [11]. In the same spectra such a marked broadening for the C-5 triazole resonance was observed so that, in some cases, its frequency was not readily determinable with precision. This effect, also observed for the C-4 resonance, although to a minor extent, weakened considerably by *N*-methyl substitution and could be mainly ascribed to prototropic tautomerism. This observation also suggested the triazole-benzotriazole structure **A**, in which tautomerism, evidenced by broadened carbon resonances, occurred on the 1,2,3-triazole ring, rather than on the tetrazepine ring.

The nitro derivative structures were assigned as follows: an AB system with J-*ortho* of 8.6 Hz in the proton spectra of **2d** and **2i**, clearly indicated the 4' position of the nitro group, while the AMX system observed for **1f** and **1n** suggested a 5' or 6' substitution, but only the former was compatible with the carbon spectra. In fact, taking into account the effects of a nitro group on a benzene ring, an agreement between the spectra of **1e** and **1f** or of **1l** and **1n** could be obtained only for a nitro group substituted in the 5' position.

The methyl group position on the nitrogen of the triazole ring for the isolated compounds **1m** and **2i** was surely derived from the existence, evidenced by a COLOC experiment, of a heteronuclear coupling between the methyl hydrogens and the C-5. It is worth noting that the same results were obtained by an NOE difference experiment, previously performed on **1m**, for the same purposes, which presented little enhancement (1%) of the H-5 signal by saturation of the triazole methyl. Such an effect was not believed probable because its smallness, probably due to the presence in the molecule of several nitrogen quadrupolar nuclei and to the difficulty of an effective degassing of the dimethyl sulfoxide solution.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage and are uncorrected. The ir spectra in nujol mulls were recorded on a PerkinElmer Model 1310 spectrometer. The ^1H-nmr spectra were recorded with a Varian EM 360 spectrometer operating at 60 MHz. The spectra of compounds **2** and **2a-e** were recorded in dimethyl sulfoxide-d_6 with a Bruker AC 200 instrument, operating at 200 MHz for the ^1H and 50 MHz for the ^{13}C. In all cases the chemical shifts were in δ units from TMS as an internal standard. The assignments were confirmed by heteronuclear correlation spectroscopy experiments, performed by using the standard Bruker programs. The COLOC experiments were optimized for a J value of 5 Hz (100 ms delay). Mass spectra were performed with a Hewlett Packard MS/System 5988. Elemental analyses (C,H,N) were performed on a Carlo Erba Elemental Analyzer Model 1106 apparatus. Short distillations were performed in a Buchi GKR 50 tubular oven.

1-(2-Nitrophenyl)-4-carboxamido-5-amino-1*H*-1,2,3-triazole (**1a**).

To an ice-cooled (0-5°) and stirred solution of sodium ethoxide (0.37 g, 16 mmoles of sodium) in 45 ml of anhydrous ethanol, cyanacetamide (1.34 g, 16 mmoles) was added; after 15 minutes, to the suspension obtained a solution of *o*-nitrophenylazide (2.38 g, 14.5 mmoles) in 45 ml of anhydrous ethanol was added dropwise. After 1 hour the ice-bath was removed and stirring was continued for 22 hours at room temperature; the solvent was evaporated *in vacuo* at temperature <50° and the residue was treated with water. The suspension obtained was washed with chloroform and the solid, consisting of the title compound, was collected by filtration, 1.97 g, 55% yield, mp 262-265° from ethanol; ir: ν 2.94, 3.07, 3.17 (NH_2), 6.10 ($CONH_2$) μ; ms: m/z (%): 248 (M^+, 18), 202 (100), 130 (49), 90 (39); ^1H nmr: δ 8.27 (dd, 1H, 3'-H, J = 7.93 and 1.63 Hz), 7.97 (ddd, 1H, 5'-H, J = 7.62, 7.59 and 1.63 Hz), 7.86 (ddd, 1H, 4'-H,

J = 7.93, 7.59 and 1.65 Hz), 7.77 (dd, 1H, 6'-H, J = 7.62 and 1.65 Hz), 7.31 and 6.51 (2 bs, 4H, $2NH_2$); ^{13}C nmr: δ 163.9 (C=O), 146.1 (4-C), 144.9 (2'-C), 134.6 (5'-C), 131.4 (4'-C), 129.6 (6'-C), 127.1 (1'-C), 125.5 (3'-C), 120.9 (5-C).

Anal. Calcd. for $C_9H_8N_6O_3$: C, 43.55; H, 3.25; N, 33.86. Found: C, 43.54; H, 3.29; N, 34.18.

4-Carboxamido-5-(2-nitroanilino)-1,2,3-triazole (**1b**).

A) A solution of 1.0 g of **1a** in 100 ml of ethanol was heated under reflux for 6 hours. The solvent was evaporated *in vacuo* to give the title compound **1b** as a yellow solid residue, 0.972 g, 97% yield, mp 260-265° dec from ethanol; ir: ν 2.98-3.22, (NH), 5.92 ($CONH_2$) μ; ms: m/z (%) 248 (M^+, 20), 202 (100), 130 (28), 90 (28); ^1H nmr: δ 8.64 (dd, 1H, 6'-H, J = 8.68 and 1.24 Hz), 8.21 (dd, 1H, 3'-H, J = 8.47 and 1.60 Hz), 7.74 (ddd, 1H, 5'-H, J = 8.68, 7.12 and 1.60 Hz), 7.04 (ddd, 1H, 4'-H, J = 8.47, 7.12 and 1.24 Hz), 11.38 and 7.55 (2 bs, 4H, 2NH and NH_2); ^{13}C nmr: δ 163.3 (C=O), 147.0 (4-C), 137.4 (2'-C), 136.1 (5'-C), 133.6 (1'-C), 126.8 (5'-C), 125.9 (3'-C), 119.3 (4'-C), 118.1 (6'-C).

Anal. Calcd. for $C_9H_8N_6O_3$: C, 43.55; H, 3.25; N, 33.86. Found: C, 43.18; H, 3.35; N, 33.57.

B) Preparation of **1a** starting from 3.85 g (23.5 mmoles) of *o*-nitrophenyl azide: provided 1.70 g, 29% yield of **1a**. Acidification of the aqueous alkaline mother liquors precipitated crude **1b** as a red solid (0.81 g, 14% yield) which was collected by filtration and purified by crystallization.

1-(2-Aminophenyl)-4-carboxamido-5-amino-1*H*-1,2,3-triazole (**1c**).

A solution of **1a** (1.60 g, 6.45 mmoles) in 200 ml of methanol was hydrogenated at room temperature and pressure in the presence of 5% palladium on activated charcoal (0.160 g). The catalyst was filtered off, washed with methanol and the combined filtrates were evaporated *in vacuo* at room temperature to give **1c**, 1.25 g, 89% yield, mp 189-191° from ethyl acetate/petroleum-ether 60-80°; ir: ν 3.03, 3.17 (NH_2), 5.71 ($CONH_2$) μ, ms: m/z (%) 214 (M^+, 56), 173 (53), 146 (53), 118 (86), 92 (65), 65 (100); ^1H nmr: δ 7.24 (ddd, 1H, 4'-H, J = 8.18, 7.24 and 1.57 Hz), 7.09 (dd, 1H, 6'-H, J = 7.85 and 1.57 Hz), 6.93 (dd, 1H, 3'-H, J = 8.18 and 1.36 Hz), 6.71 (ddd, 1H, 5'H, J = 7.85, 7.24 and 1.36 Hz), 7.85, 7.20 and 5.96 (3 bs, 6H, $3NH_2$); ^{13}C nmr: δ 164.2 (C=O), 145.0 (5-C), 143.9 (2'-C), 130.4 (4'-C), 127.3 (6'-C), 121.3 (4-C), 119.0 (1'-C), 116.4 (3'-C), 116.3 (5'-C).

Anal. Calcd. for $C_9H_{10}N_6O$: C, 49.53; H,4.62; N, 38.52. Found: C, 49.64; H, 4.54; N, 38.51.

4-Carboxamido-5-(2-aminoanilino)-1,2,3-triazole (**1d**).

A solution of **1b** (0.900 g, 3.63 mmoles) in 200 ml of ethanol was hydrogenated at room temperature and pressure in the presence of 5% palladium on activated charcoal (0.120 g). The catalyst was filtered off, washed with ethanol and the combined filtrates were evaporated *in vacuo* to give the title compound, 0.840 g, 96% yield, mp 180-182° from ethanol; ir: ν 2.94-3.17 (NH, NH_2), 5.99 ($CONH_2$) μ; ms, m/z (%) 218 (M^+, 100), 173 (33), 145 (43), 118 (95), 92 (48), 65 (59); ^1H nmr: δ 6.85-6.63 (m, 4H, 3'-H, 4'-H, 5'-H and 6'-H) 8.05 and 7.48 (2 bs, 4H, 2 NH_2), 7.67 and 7.63 (2 bs, 2H, 2 NH); ^{13}C nmr: δ 164.1 (C=O), 149.0 (5-C), 137.5 (2'-C), 128.9 (4-C), 124.7 (1'-C), 121.8 (5'-C) 118.0 (4'-C), 117.4 (6'-C), 116.4 (3'-C).

Anal. Calcd. for $C_9H_{10}N_6O$: C, 49.53; H, 4.62; N, 38.52. Found: C, 49.77; H, 4.41; N, 38.86.

4-(Benzotriazol-1-yl)-5-carboxamido-1,2,3-triazole (**1e**).

A) To an ice-cooled and stirred solution of **1c** (1.22 g, 5.6 mmoles) in 30 ml of 10% sulfuric acid, a solution of sodium nitrite (0.423 g, 6.1 mmoles) in 10 ml of water was added dropwise. Immediately **1e** precipitated as a crystalline solid which, after 15 minutes, was collected by filtration, 1.26 g, 99% yield, mp 254-256° from ethanol; ir: ν 2.98, 3.15 (NH_2), 3.22 (NH), 6.02 ($CONH_2$) μ; ms: m/z (%) 229 (M^+, 4), 173 (16), 103 (100), 76 (75).

Anal. Calcd. for $C_9H_7N_7O$: C, 47.16; H, 3.08; N, 42.78. Found: C, 46.83; H, 2.91; N, 42.44.

B) To an ice-cooled (0-5°) and stirred solution of **1d** (1.28 g, 5.87 mmoles) in 60 ml of 18% hydrochloric acid, a solution of sodium nitrite (0.527 g, 7.6 mmoles) in ≈30 ml of water was added dropwise. After 1 hour the ice-bath was removed, the stirring was continued for 2 hours at room temperature and **1e**, precipitated as a crystalline solid, was collected by filtration, 1.29 g, 96% yield, mp 253-255° from ethanol.

4-[5-(Nitro)benzotriazol-1-yl]-5-carboxamido-1,2,3-triazole (**1f**).

To an ice-cooled and stirred solution of **1e** (0.343 g, 1.5 mmoles) in 3 ml of concentrated sulfuric acid, potassium nitrate (0.306 g, 3.0 mmoles) was added portionwise (≈1 hour). The ice-bath was removed and stirring was continued for 1 hour at room temperature and for 1 hour at 60°. The mixture was poured into crushed ice and the mononitro derivative **1f** separated as a pale yellow solid, 0.315 g, 77% yield; mp 238-240° from ethanol/water; ir: ν 2.98 (NH), 5.98 ($CONH_2$), 6.56, 7.41 (NO_2) μ; ms: m/z (%) 274 (M^+, 4), 228 (31), 200 (26), 148 (84), 103 (58), 75 (100).

Anal. Calcd. for $C_9H_6N_8O_3$: C, 39.42; H, 2.21; N, 40.87. Found: C, 39.75; H, 2.45; N, 41.01.

4-(Benzotriazol-1-yl)-5-carboxy-1,2,3-triazole (**1g**).

A) A solution of **1e** (0.300 g, 1.3 mmoles) and 1.5 g of sodium hydroxide in 20 ml of dioxane-water 1:1 was refluxed for 20 hours. The solvent was evaporated *in vacuo*, the residue was dissolved in water and the solution was acidified (*p*H ≈ 3) to precipitate **1g** as a white solid, 0.227 g, 76% yield, mp 195-197° from water; ir: ν 3.20 (NH) 4.0 broad (OH), 5.85 (COOH), μ; ms: m/z (%) 230 (M^+, 2), 174 (21), 103 (88), 76 (100).

Anal. Calcd. for $C_9H_6N_6O_2$: C, 46.96; H, 2.63; N, 36.51. Found: C, 46.93; H, 2.43; N, 36.67.

B) A solution of **1e** (1.300 g, 5.70 mmoles) in 20 ml of 50% sulfuric acid was heated at 110° for 22 hours. Concentrated ammonia solution was added dropwise to decrease solution acidity (*p*H ≈ 3) and **1g** precipitated as a crystalline solid which was collected and washed with water, 0.868 g, yield 67%, mp 196-198° from water.

4-(Benzotriazol-1-yl)-5-carboethoxy-1,2,3-triazole (**1h**).

A solution of **1g** (0.200 g, 0.87 mmoles) and two drops of concentrated sulfuric acid in 20 ml of anhydrous ethanol was refluxed for 30 hours. The solvent was concentrated *in vacuo* and the residue was treated with water to give a crude precipitate which was purified by crystallization from benzene, 0.135 g, 60% yield; mp 120-123°; ir: ν 5.75 (COOEt) μ; ms: m/z (%) 268 (M^+, 7), 202 (19), 103 (100), 76 (83).

Anal. Calcd. for $C_{11}H_{10}N_6O_2$: C 51.16; H, 3.90; N 32.55. Found: C, 50.89; H, 3.84; N, 32.80.

Mixture of 1- and 2-Methyl-4-(Benzotriazol-1-yl)-5-carboxy-1,2,3-triazole (**1i**).

To a stirred mixture of anhydrous potassium carbonate (0.215 g, 1.55 mmoles) and dimethyl sulfate (0.44 ml, 4.6 mmoles) in 5 ml of anhydrous acetone, a solution of the ester **1h** (0.200 g, 0.77 mmole) in 20 ml of anhydrous acetone was added dropwise. Stirring was continued at room temperature for 6 hours then the solvent was evaporated and the residue was treated with water. The title compound separated as a solid residue from the acid solution and was collected by filtration, 0.120 g, 65% yield, crystallization from water gave a solid mixture with mp 161-164°; ir: ν 4.08, 5.40 (combination bands), 5.81 (COOH) μ.

Anal. Calcd. for $C_{10}H_8N_6O_2$: C, 49.18; H, 3.30; N, 34.42. Found: C, 48.84; H, 3.26; N, 34.73.

4-(Benzotriazol-1-yl)-1,2,3-triazole (**1l**).

A solution of 0.130 g of **1g** in 1.5 ml of dimethylformamide was heated under reflux for 4 hours. Dilution with water precipitated **1l** as a crystalline solid which was collected by filtration, 0.092 g, 87% yield, mp 220-223° from ethyl acetate/petroleum ether 60-80°; ir: ν 3.22 (NH) μ; ms: m/z (%) 186 (M^+, 18), 158 (44), 103 (93), 76 (100).

Anal. Calcd. for $C_8H_6N_6$: C, 51.61; H, 3.25; N, 45.14. Found: C, 51.28; H, 2.99; N, 44.98.

1-Methyl-4-(benzotriazol-1-yl)-1*H*-1,2,3-triazole (**1m**).

To a solution of sodium hydroxide (0.060 g, 1.5 mmoles) in 10 ml of methanol, **1l** (0.186 g, 1.0 mmole) and iodomethane (1 ml, 16.0 mmoles) were added and the mixture was stirred at room temperature for 1 night. The solvent was evaporated *in vacuo* and the solid residue, consisting of the crude **1m**, was washed with 10% sodium hydroxide and water; crystallization from benzene gave 0.120 g, 60% yield, mp 172-174°; ms: m/z (%) 200 (M^+, 7), 144 (11), 117 (21), 103 (43), 76 (23), 42 (100).

Anal. Calcd. for $C_9H_8N_6$: C, 53.99; H, 4.03; N, 41.98. Found: C, 53.95; H, 4.18; N, 42.35.

4-[5-(Nitro)-benzotriazol-1-yl]-1,2,3-triazole (**1n**).

To an ice-cooled and stirred solution of **1l** (0.200 g, 1.1 mmoles) in 2 ml of concentrated sulfuric acid, potassium nitrate (0.224 g, 2.2 mmoles) was added portionwise (≈ 1 hour). The ice-bath was removed and stirring was continued for 3 hours at 60°. The mixture was poured into crushed ice and the mononitro derivative **1n** separated as a pale yellow solid, 0.204 g, 80% yield, mp 231-235° from ethanol/water 1:2; ir: ν 6.62, 7.41 (NO_2) μ; ms: m/z (%) 231 (M^+, 43), 173 (21), 148 (50), 129 (74), 102 (98), 75 (100).

Anal. Calcd. for $C_8H_5N_7O_2$: C, 41.57; H, 2.18; N, 42.41. Found: C, 41.60; H, 2.19; N, 41.19.

4-Carboxy-5-(2-nitroanilino)-1,2,3-triazole (**1o**).

A solution of **1b** (0.450 g, 1.8 mmoles) in 30 ml of 10% sodium hydroxide was heated under reflux for 6 hours. Acidification with concentrated hydrochloric acid precipitated **1o** as an orange soft solid which was collected and washed with water, 0.335 g, 74% yield, mp 173-174° dec, yellow needles from dimethylformamide/water; ir: ν 2.94, 3.12 (NH), 5.74 (COOH), μ; ms: m/z (%) 249 (M^+, 6), 205 (100), 138 (88), 92 (59), 65 (65); ^1H nmr: δ 8.64 (dd, 1H, 6'-H, J = 8.57 and 0.95 Hz), 8. 19 (dd, 1H, 3'-H, J = 8.48 and 1.41 Hz), 7.72 (ddd, 1H, 5'-H, J = 8.57, 7.16 and 1.41 Hz), 7.04 (ddd, 1H, 4'-H, J = 8.48, 7.16 and 0.95 Hz), 11.06 (bs, 3H, 2NH and COOH); ^{13}C nmr: δ 162.5 (C=O), 148.0 (5-C), 137.4 (2'-C), 136.2 (5'-C), 133.7 (1'-C), 126.4 (4-C), 125.9 (3'-C), 119.6 (4'-C), 118.2 (6-C).

Anal. Calcd. for $C_9H_7N_5O_4$: C, 43.38; H, 2.83; N, 28.10. Found: C, 43.19; H, 2.96; N, 27.86.

4-Carboxy-5-(2-aminoanilino)-1,2,3-triazole (**1p**).

A solution of **1o** (0.223 g, 0.89 mmole) in 150 ml of ethanol was hydrogenated at room temperature and pressure in the presence of 5% palladium on activated charcoal (0.100 g). The reaction mixture was worked up as described for the preparation of **1d**, 0.190 g, 97% yield, mp 172-174° from dimethylformamide/water; ir: ν 3.03, 3.92, 4.88 (NH, combination bands), 6.25 (COO^-) μ; ms: m/z (%) 219 (M^+, 2), 175 (33), 146 (29), 119 (52), 65 (41), 44 (100); ^1H nmr: δ 6.91-6.69 (m, 4H, 3'-H, 4'-H, 5'-H and 6'-H), 7.68, 7.65 and 7.61 (3 bs, 5H, 2 NH, NH_2 and COOH); ^{13}C nmr: δ 163.3 (C=O), 150.0 (5-C), 137.0 (2'-C), 129.0 (4-C), 122.6 (5'-C), 122.1 (1'C), 119.0 (4'-C), 118.9 (6'-C) 117.3 (3'-C).

Anal. Calcd. for $C_9H_9N_5O_2$: C, 49.31; H, 4.14; N, 31.95. Found: C, 49.28; H, 4.26; N, 31.60.

4-(2-Nitroanilino)-1,2,3-triazole (**1q**).

A solution of 0.300 g of **1o** in 15 ml of toluene and 2 ml of dimethylformamide was heated under reflux for 8 hours. The solvent was evaporated *in vacuo* and the residue was treated with water and 6% sodium hydrogen carbonate. The insoluble yellow solid consisted of **1q**, 0.235 g, 95% yield, mp 202-205° from ethanol; ir: ν 3.07, 3.20 (NH) μ; ms: m/z (%) 205 (M^+, 100), 103 (28), 77 (48); ^1H nmr: δ 8.13 (dd, 1H, 3'-H, J = 8.51 and 1.36 Hz), 7.84 (s, 1H, 4-H), 7.70 (dd, 1H, 6'-H, J = 8.56 and 1.26 Hz); 7.59 (ddd, 1H, 5'-H, J = 8.56, 6.92 and 1.36 Hz), 6.92 (ddd, 1H, 4'-H, J = 8.51, 6.92 and 1.26 Hz), 9.60 (bs, 2H, 2NH); ^{13}C nmr: δ 144.4 (5-C), 140.4 (2'-C), 136.0 (5'-C), 133.1 (1'-C), 125.8 (3'-C), 123.2 (4-C), 118.2 (4'-C), 116.8 (6-C).

Anal. Calcd. for $C_8H_7N_5O_2$: C, 46.83; H, 3.44; N, 34.13. Found: C, 46.92; H, 3.58; N, 34.26.

4-(2-Aminoanilino)-1,2,3-triazole (**1r**).

A solution of **1q** (0.205g, 1.0 mmole) in 50 ml of ethanol was hydrogenated at room temperature and pressure in the presence of 5% palladium on activated charcoal (0.030 g). The reaction mixture was worked up as described for the preparation of **1d**, 0.170 g, 97% yield, mp 135-136° from water; ir: ν 2.94, 3.28 (NH, NH_2); ms: m/z (%) 175 (M^+, 100), 131 (30), 119 (38), 92 (30); ^1H nmr: δ 6.72-6.50 (m, 4H, 3'-H, 4'-H, 5'-H and 6'-H), 7.30 and 7.26 (2 bs, 4H, 2 NH and NH_2); ^{13}C nmr: δ 149.0 (5-C), 137.5 (2'-C), 129.6 (4-C), 121.0 (1'-C), 121.0 (5'-C), 116.9 (4'-C), 116.8 (6'-C), 115.1 (3'-C).

Anal. Calcd. for $C_8H_9N_5$: C, 54.85; H, 5.18; N, 39.98. Found: C, 54.85; H, 5.03; N, 40.34.

1-(2-Nitro-4-methylphenyl)-4-carboxamido-5-amino-1*H*-1,2,3-triazole (**2a**).

This compound was prepared as described above for **1a** starting from 2-nitro-4-methylphenyl azide [8], 70% yield, mp 272-273° from ethanol; ir: ν 2.94, 3.07, 3.17 (NH_2), 6.02 ($CONH_2$) μ; ms: m/z (%) 262 (M^+, 25), 216 (100), 144 (22). ^1H nmr: δ 8.11 (d, 1H, 3'-H, J = 1.69 Hz), 7.77 (dd, 1H, 5'-H, J = 1.69 and 8.18 Hz), 7.63 (d, 1H, 6'-H, J = 8.18 Hz), 7.25 and 6.43 (2 bs, 4H, 2 NH_2), 2.53 (s, 3H, CH_3); ^{13}C nmr: δ 164.2 (C=O), 146.0 (4-C), 142.0 (2'-C), 139.8 (4'-C), 134.9 (5'-C), 129.3 (6'-C), 126.8 (1'-C), 125.5 (3'-C), 120.7 (5-C), 20.3 (CH_3).

Anal. Calcd. for $C_{10}H_{10}N_6O_3$: C, 45.80; H, 3.84; N, 32.05. Found: C, 45.54; H, 3.65; N, 31.83.

1-(2-Amino-4-methylphenyl)-4-carboxamido-5-amino-1*H*-1,2,3-triazole (**2b**).

This compound was prepared as described above for **1c**, 98% yield, mp 188-189° from ethyl acetate; ir: ν 3.05, 3.15 (NH_2), 6.06 ($CONH_2$) μ; ms: m/z (%) 232 (M^+, 13), 160 (29), 133 (50) 77 (100); ^1H nmr: δ 6.96 (d, 1H, 6'-H, J = 7.97 Hz), 6.74 (d, 1H, 3'-H, J = 1.91 Hz), 6.53 (dd, 1H, 5'-H, J = 7.97 and 1.91 Hz), 7.20, 5.91 and 4.94 (3 bs, 6H, 3 NH_2), 2.26 (s, 3H, CH_3); ^{13}C nmr: δ 164.2 (C=O), 145.0 (4-C), 143.6 (2'-C), 140.0 (4'-C), 127.0 (6'-C), 121.3 (5-C), 117.3 (3'-C), 116.8 (1'-C), 116.6 (5'-C), 20.8 (CH_3).

Anal. Calcd. for $C_{10}H_{12}N_6O$: C, 51.71; H, 5.21; N, 36.19. Found: C, 51.79; H, 5.29; N, 36.26.

4-[5-(Methyl)benzotriazol-1-yl]-5-carboxamido-1,2,3-triazole (**2c**).

This compound was prepared as described above for **1e**, 67% yield, mp 251-254° dec from ethanol; ir: ν 3.03, 3.17 (NH_2), 3.22 (NH), 5.99 ($CONH_2$) μ; ms: m/z (%) 243 (M^+, 6), 187 (18), 117 (100), 89 (75).

Anal. Calcd. for $C_{10}H_9N_7O$: C, 49.38; H, 3.73; N, 40.31. Found: C, 49.25; H, 3.66; N, 40.40.

4-[(4-Nitro-5-methyl)benzotriazol-1-yl]-5-carboxamido-1,2,3-triazole (**2d**).

This compound was prepared as described above for **1f**, 84% yield, mp 256-259° dec from ethanol/water; ir: ν 3.03 (NH), 5.98 ($CONH_2$), 6.58, 7.46 (NO_2) μ; ms: m/z (%) 288 (M^+, 4), 232 (99), 162 (37), 116 (99), 89 (100).

Anal. Calcd. for $C_{10}H_8N_8O_3$: C, 41.67; H, 2.80; N, 38.88. Found: C, 42.01; H, 2.79; N, 38.66.

4-[5-(Methyl)benzotriazol-1-yl]-5-carboxy-1,2,3-triazole (**2e**).

This compound was prepared as described above for **1g**, 99% yield, mp 180-182° from water; ir: ν 4.0 broad (OH), 5.81 (COOH), μ; ms: m/z (%) 244 (M^+, 1), 171 (87), 117 (70), 89 (100).

Anal. Calcd. for $C_{10}H_8N_6O_2$: C, 49.18; H, 3.30; N, 34.42. Found: C, 49.48; H, 3.31; N, 34.08.

4-[5-(Methyl)benzotriazol-1-yl]-1,2,3-triazole (**2f**).

This compound was prepared as described above for **1l**, 95% yield, mp 191-193° from ethyl acetate; ir: ν 3.22 (NH) μ; ms: m/z (%) 200 (M^+, 27), 171 (100), 117 (46), 89 (79).

Anal. Calcd. for $C_9H_8N_6$: C, 53.99; H, 4.03; N, 41.98. Found. C, 54.30; H, 4.23; N, 42.18.

4-[5-(Methyl)benzotriazol-1-yl]-5-carboethoxy-1,2,3-triazole (**2g**).

A solution of **2e** (0.200 g, 0.82 mmole) in 6 ml of thionyl chloride was refluxed for 4 hours; after evaporation of the reagent *in vacuo*, 15 ml of anhydrous ethanol was added and the mixture was refluxed for 4 hours. Evaporation of the solvent and treatment with water gave a crude precipitate which was purified by crystallization from benzene, 0.150 g, 67% yield, mp 141-143°; ir: ν 5.75 (COOEt) μ; ms: m/z (%) 272 (M^+, 8), 171 (21), 117 (95), 89 (100).

Anal. Calcd. for $C_{12}H_{12}N_6O_2$: C, 52.93; H, 4.44; N, 30.87. Found: C, 53.16; H, 4.58; N, 30.85.

Mixture of 1-and 2-Methyl-4-[5-(methyl)benzotriazol-1-yl]-5-carboethoxy-1,2,3-triazole (**2h**).

This compound was prepared as described above for **1i**. Crystallization from benzene gave a mixture (21% yield) with mp 78-82°; ir: ν 6.2 (COOEt) μ.

Anal. Calcd. for $C_{13}H_{14}N_6O_2$: C, 54.54; H, 4.89; N, 29.37. Found: C, 54.68; H, 5.01; N, 29.55.

4-[(4-Nitro-5-methyl)benzotriazol-1-yl]-1,2,3-triazole (**2i**).

To an ice-cooled and stirred solution of **2f** (0.150 g, 0.75 mmole) in 1.5 ml of concentrated sulfuric acid, nitric acid (1.5 ml, d 1.40) was added dropwise. The ice-bath was removed and stirring was continued for 2 hours at 100°. The mixture was poured into crushed ice to precipitate **2i** which was collected by filtration and washed with water, 0.216 g, 88% yield, mp 241° dec from ethyl acetate/petroleum ether 60-80°; ir: ν 6.62, 7.41 (NO_2) μ; ms: m/z (%) 245 (M^+, 71), 172 (23), 116 (48), 89 (86), 63 (100).

Anal. Calcd. for $C_9H_7N_7O_2$: C, 44.08; H, 2.88; N, 39.99. Found: C, 44.04; H, 2.77; N, 39.58.

1-Methyl-4-[(5-methyl)benzotriazol-1-yl]-1*H*-1,2,3-triazole (**2l**).

This compound was prepared as described above for **1m**, 56% yield, mp 207-209° from benzene; ms: m/z (%) 214 (M^+, 9), 117 (59), 89 (30), 42 (100).

Anal. Calcd. for $C_{10}H_{10}N_6$: C, 56.06; H, 4.71; N, 39.23. Found: C, 55.99; H, 4.56; N, 39.53.

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