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SYNTHESIS OF NITROGEN-HETEROCYCLIC ANALOGS OF L-ASCORBIC ACID: A TRIAZOLYL ANALOG AND ITS REACTIONS*

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ABSTRACT

A triazolyl analog of dehydro-L-ascorbic acid (also a *C*-nucleoside analog) was prepared. The reaction of 4-formyl-2-phenyl-1,2,3-triazole with glyoxal in the presence of potassium cyanide, through an acyloin condensation followed by a cyanohydrin reaction, gave 2,5-dihydro-3,4-dihydroxy-5-imino-2-(2-phenyl-1,2,3-triazol-4-yl)-5(2*H*)-furanone (**6**) that gave a monoacetyl derivative. Reaction of **6** with nitrous acid afforded 2,3-dioxo-4-(2-phenyl-1,2,3-triazol-4-yl)butano-1,4-lactone (**10**) that, upon reaction with phenyl- or (*p*-nitrophenyl)-hydrazine, gave the 4-(2-phenyl-1,2,3-triazol-4-yl)butano-1,4-lactone 2,3-bis(arylhydrazones) (**12** or **13**). Rearrangement of **12** gave hydroxy-[1-phenyl-4-(phenylhydrazono)-2-pyrazolin-5-one-3-yl]-(2-phenyl-1,2,3-triazol-4-yl)methane (**16**), which gave a monoacetyl derivative. Treatment of **6** with phenylhydrazine in aqueous acetic acid gave [1-phenyl-4-(phenylhydrazono)-2-pyrazolin-5-one-3-yl]-(2-phenyl-1,2,3-triazol-4-yl)methane, which is the deoxygenated analog of **16**. Reaction of **10** with *o*-phenylenediamine and phenylhydrazine afforded a red product identified as 1-hydroxy-2-(phenylhydrazono)-1-(2-phenyl-1,2,3-triazol-4-yl)-2-(2-quinoxalinone-3-yl)ethane (**19**) which, upon treatment with alkali, gave hydroxy-(1-phenylflavazol-3-yl)-(2-phenyl-1,2,3-triazol-4-yl)-methane (**20**). Acetylation of **20** gave the acetoxy-(1-phenylflavazol-3-yl)-(2-phenyl-1,2,3-triazol-4-yl)methane (**21**). This sequence, **10**→**19**→**21**, confirms the initial position of the reaction of *o*-phenylenediamine with **10**. The structures of the products were deduced from their mode of preparation, chemical reactions, and spectral data.

INTRODUCTION

The importance of L-ascorbic acid lies not only in its being a vitamin, but also in its having various biological properties; *e.g.*, it is a cofactor in certain specific enzymic reactions, and is needed for various, normal functions[2,3].

C-Nucleosides[4–6] constitute a group of compounds to which considerable

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attention has been devoted during the past few years, as a consequence of their isolation from natural sources, and of their biological properties, characterized by the stability of the C–C bond, as compared with the C–N bond between the nitrogen-heterocycle and the sugar moiety. Attention has thus been attracted to devising approaches[6] to their synthesis, as well as that of various analogs.

In previous reports in this series, we have described various synthetic approaches to the synthesis of polyhydroxyalkyl nitrogen-heterocycles[7-17] of the *C*-nucleoside type, as well as the role of the carbohydrates as heterocyclic precursors[18-27]. Such heterocyclizations, achieved through the use of hydrazines or *ortho*-diamines as a source of nitrogen, afford derivatives capable of further transformations. The carbohydrate precursors were either monosaccharides, kojic acid, or L-ascorbic acid and its hydroxyalkyl and aryl analogs.

In continuation of our work on the synthesis of L-ascorbic acid analogs and their ring transformation into nitrogen heterocycles, and in view of the aspects just described, we now report the synthesis of a heterocyclic analog of L-ascorbic acid, namely, a triazolyl analog; it is also a new *C*-nucleoside analog containing in its sugar moiety an enediolic system, a unique feature of L-ascorbic acid.

DISCUSSION

Synthesis of L-ascorbic acid and its analogs may be achieved in various ways[3,28]. The method of Dahn and coworkers[29-31] for the synthesis of aryl analogs was used in the present investigation; reaction of glyoxal, in the presence of cyanide ion, with the aldehyde bearing the desired aryl group afforded the required analog. The aldehyde, namely, 4-formyl-2-phenyl-1,2,3-triazole (**2**), needed for the synthesis of the target compound (**6**), was conveniently prepared[32] by periodate oxidation of 2-phenyl-4-(D-*arabino*-tetritol-1-yl)-1,2,3-triazole (**1**). Reaction of aldehyde **2** with glyoxal in the presence of cyanide ion afforded compound **6**.

A mechanism similar to that postulated for the aryl analogs[29] may be involved, wherein an acyloin condensation of **2** with the glyoxal, catalyzed by the cyanide ion, gives the glycosulose intermediate **3**, which, on reaction with cyanide, gives the cyanohydrin **4**, and this cyclizes to **5**; compound **5** then tautomerizes to **6**. This shows the dual role of the cyanide ion, as a catalyst and as a reactant, and so it should be present in concentrations higher than the equivalent in order to provide a good yield. Compound **6** gave the color reaction characteristic of an enediol[29], and its elemental analysis agreed with that calculated for $C_{12}H_{10}N_4O_3$, corresponding to **6**. Its infrared (i.r.) spectrum showed the presence of hydroxyl absorption at 3600 cm^{-1}, NH absorption at 3400 cm^{-1}, and bands at 1710 cm^{-1} (corresponding to a carbonyl absorption) and at 1640 cm^{-1} due to C=C and C=N; this may be ascribed to tautomerization of the enediol **6** to the hydroxycarbonyl compound **5**. The n.m.r. spectrum of **6** showed hydroxyl protons, as a broad singlet, at δ 5.2, that disappeared on addition of D_2O; the CH proton of the furanone nucleus appeared as a singlet

at δ 6.7, and the aromatic protons as a multiplet at δ 7.3–8.8, in addition to the imino proton at δ 9.6 (exchangeable with D_2O).

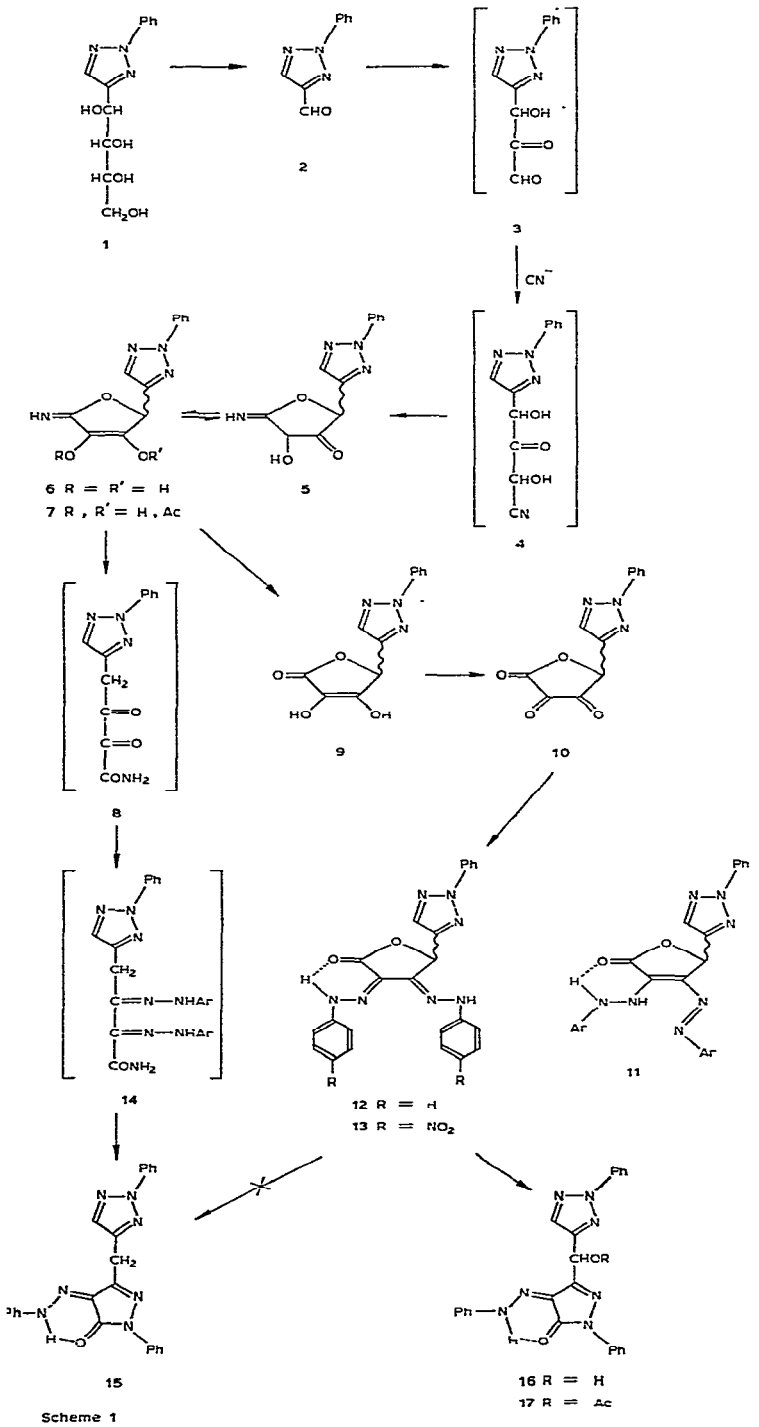
Acetylation of the iminolactone **6** with acetic anhydride afforded the monoacetyl derivative **7**, which may result from **6** or one of its tautomers. Its i.r. spectrum showed a band at 1740 cm^{-1} indicating the presence of an acetyl group, in addition to bands appearing in the carbonyl-frequency region.

Treatment of **6** with nitrous acid resulted in hydrolysis of the imino group, to afford **9**, and simultaneous oxidation of the enediol grouping, to afford the dehydro derivative 2,3-dioxo-4-(2-phenyl-1,2,3-triazol-4-yl)butano-1,4-lactone (**10**). Similar dioxo compounds could be readily reduced to the corresponding enediol.

Reaction of **10** with phenylhydrazine gave 4-(2-phenyl-1,2,3-triazol-4-yl)-butano-1,4-lactone 2,3-bis(phenylhydrazone) (**12**), which was characterized by its red color, and the presence in its i.r. spectrum of a band at 1715 cm^{-1} for the lactone carbonyl group and the absence of the two carbonyl frequencies appearing in the i.r. spectrum of **10** at 1710 and 1690 cm^{-1}. The shift of the lactone carbonyl band for the bishydrazone **12** to lower frequency (1715 cm^{-1}) rather than **10** (at 1770 cm^{-1}) could be attributed to its hydrogen bonding with the imino proton of the hydrazone residue, being similar in this respect to the bishydrazones of L-ascorbic acid and its analogs.

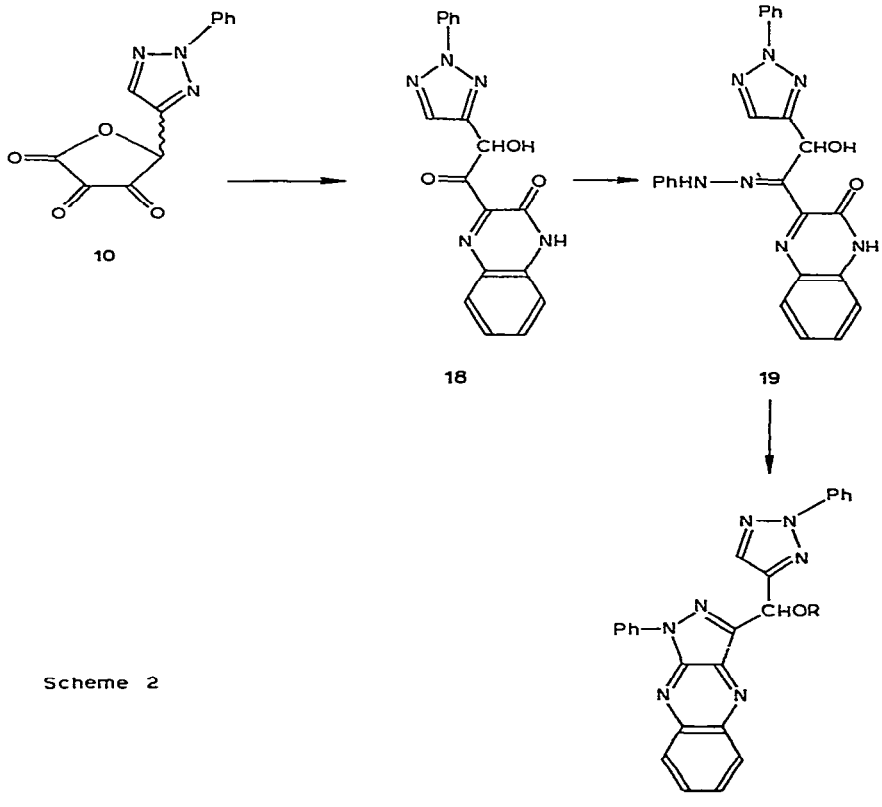
The reaction was successfully extended by using (*p*-nitrophenyl)hydrazine, whereby 4-(2-phenyl-1,2,3-triazol-4-yl)butano-1,4-lactone 2,3-bis[(*p*-nitrophenyl)hydrazone] (**13**) was prepared; it showed a lactone band at 1720 cm^{-1}, indicating similar hydrogen-bonding. The structure of the reaction product of phenylhydrazine with dehydro-L-ascorbic acid was recently[33] revised to 2,3-dideoxy-3-(phenylazo)-2-(phenylhydrazono)-L-*threo*-hex-2-enone-1,4-lactone, rather than L-*threo*-2,3-hexodiulosono-1,4-lactone 2,3-bis(phenylhydrazone). Compounds **12** and **13** should have a similar structure; consequently, their existence as the azohydrazino structure **11** cannot be rejected.

Rearrangement of the red bis(phenylhydrazone) **12** to hydroxy-[1-phenyl-4-(phenylhydrazono)-2-pyrazolin-5-one-3-yl]-(2-phenyl-1,2,3-triazol-4-yl)methane (**16**) was achieved by using alkali, followed by acidification, which resulted in the opening of the lactone ring to afford the corresponding carboxylate intermediate; this underwent simultaneous ring-closure *via* nucleophilic attack of the imino group of the hydrazone residue on the carboxylate carbonyl group. The orange color of the resulting 2-pyrazolinone **16** was characteristic of such compounds, and its i.r. spectrum showed a band at 1660 cm^{-1} due to the OCN group (instead of the lactone band at 1715 cm^{-1}, appearing in the spectrum of its precursor). The presence of a hydroxyl group in **16** was indicated by a hydroxyl absorption at 3400 cm^{-1}, and this was confirmed by formation of the monoacetate **17** on treatment with acetic anhydride–pyridine; in its i.r. spectrum, compound **17** showed a band for acetyl at 1730 cm^{-1}, in addition to amide absorption at 1660 cm^{-1}, and it was formulated as acetoxy-[1-phenyl-4-(phenylhydrazono)-2-pyrazolin-5-one-3-yl]-(2-phenyl-1,2,3-triazol-4-yl)-methane.



Scheme 1

On the other hand, when compound **6** reacted with phenylhydrazine in aqueous acetic acid, it gave an orange product, **15**, that differed from the bis(hydrazone) **12** and from its rearranged 2-pyrazolinone **16**. In its i.r. spectrum, compound **15** showed a band at 1660 cm^{-1}, but no other band in the carbonyl-frequency region. Its elemental analysis agreed with that calculated for $C_{24}H_{19}N_4O$, containing one oxygen less than **16**. Moreover, it failed to give an acetyl derivative under conditions similar to those used for the preparation of **17**, indicating the absence of the hydroxyl group present in **16**. Consequently, it was formulated as [1-phenyl-4-(phenylhydrazono)-2-pyrazolin-5-one-3-yl]-(2-phenyl-1,2,3-triazol-4-yl)methane. Comparison of this reaction with the reaction sequence **10**→**12**→**16** indicated that, for the formation of **15**, hydrolysis accompanied by deoxygenation occurred, primarily affording a deoxygenated intermediate, of probable structure **8** (not isolated); this was followed by reaction of **8** with phenylhydrazine, to give the corresponding bis(hydrazone), and this cyclized to **15** by nucleophilic attack of the nitrogen pair of electrons of hydrazone **14** on the carbonyl group, followed by loss of ammonia. These results are in accord with those for the phenyl analog, which indicated that no deoxygenation had occurred during opening of the lactone ring in the bis(phenylhydrazone) **12**.



Scheme 2

Another series of heterocyclic compounds resulting from the 5-furanone nucleus was achieved *via* reaction with *o*-phenylenediamine. Reaction of **10** with an equimolar proportion of *o*-phenylenediamine, followed by phenylhydrazine, similarly to that reported earlier, gave the mono(phenylhydrazone), namely, 1-hydroxy-2-(phenylhydrazono)-1-(2-phenyl-1,2,3-triazol-4-yl)-2-(2-quinoxalinone-3-yl)ethane (**19**); on treatment with dilute alkali, **19** afforded hydroxy-1-(phenylflavazol-3-yl)-(2-phenyl-1,2,3-triazol-4-yl)methane (**20**), readily characterized by its yellow color (whereas its precursor monophenylhydrazone was red). The i.r. spectrum of the flavazole **20** did not show any absorption in the carbonyl-frequency region, whereas its precursor **19** showed a band at 1660 cm^{-1} due to OCN of the 2-quinoxalinone ring. The presence of the hydroxyl group in the flavazole **20**, and, consequently, in its precursor **19**, was proved by its acetylation to give a product shown by its elemental analysis to have the molecular formula $C_{26}H_{21}N_7O_3$, indicating that it was the monoacetyl derivative **21**; its i.r. spectrum showed an absorption, due to the acetyl group, at 1720 cm^{-1}. This sequence of reactions from **10** to the flavazole **20** confirmed that the reaction of *o*-phenylenediamine with **10** involved the lactone carbonyl group, giving **18**, and that **18** reacts with phenylhydrazine to give **19**, as, otherwise, this sequence of reactions could not afford the flavazole **20**.

EXPERIMENTAL

General methods. — Melting points were determined with a Kofler-block apparatus and are uncorrected. I.r. spectra were recorded with a Unicam SP-200 spectrometer, and n.m.r. spectra (for solutions in pyridine-d_5), with a Jeol-100 spectrometer, with tetramethylsilane as the internal reference-standard. Microanalyses were performed in the Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt.

2,5-Dihydro-3,4-dihydroxy-2-(2-phenyl-1,2,3-triazol-4-yl)-5-imino-5-(2H)-furanone (**6**). — A cooled solution of potassium cyanide (4.2 g) in 2M aqueous sodium hydroxide (120 mL) was treated with glyoxal–sodium hydrogensulfite (10.4 g) under nitrogen; a solution of 4-formyl-2-phenyl-1,2,3-triazole (5 g) in 1,4-dioxane (9 mL) was then added in one portion. After 30 min, the nitrogen stream was stopped, and the pH was adjusted to 6 by the addition of glacial acetic acid, whereupon the product separated out in pale-yellow crystals. The mixture was stirred for a further 3 h, and the imino product was filtered off, successively washed with water and methanol, and dried (yield 45%). It was recrystallized from ethanol to give pale-yellow needles; m.p. 156–158°; ν_{max}^{Nujol} 3600 (OH), 3400 (NH), 1710 (CO), and 1640 cm^{-1} (C=C and C=N).

Anal. Calc. for $C_{12}H_{10}N_4O_3$: C, 55.8; H, 3.9; N, 21.7. Found: C, 55.6; H, 4.0; N, 22.0.

Acetylation of **6**. — A mixture of iminolactone **6** (0.5 g) and acetic anhydride (2 mL) was heated on a boiling-water bath for 10 min, and then kept for 2 h at room temperature. The mixture was poured onto crushed ice, and the acetate that separated

out was filtered off, successively washed with water and sodium hydrogencarbonate solution, and recrystallized from chloroform–ethanol, giving the monoacetate **7**; m.p. 196–198°; ν_{max}^{Nujol} 3400 (NH), 1740 (OAc), 1710 (CO), and 1640 cm^{-1} (C=N).

Anal. Calc. for $C_{14}H_{12}N_4O_4$: C, 56.0; H, 4.0; N, 18.7. Found: C, 55.7; H, 4.2; N, 18.7.

2,3-Dioxo-4-(2-phenyl-1,2,3-triazol-4-yl)butano-1,4-lactone (**10**). — A solution of compound **6** (0.2 g) in acetone (2 mL) and M sulfuric acid (4 mL) was cooled, and 10% sodium nitrite solution (3 mL) was gradually added. After standing at room temperature for 5 min, the mixture was warmed on a water bath at 50° until a clear solution was obtained. On cooling, the lactone that separated out in colorless needles was filtered off, successively washed with water and methanol, and dried (yield 60%). Recrystallization was effected from ethanol; m.p. 207°; ν_{max}^{Nujol} 1770 (COO), 1710, and 1690 cm^{-1} (CO).

Anal. Calc. for $C_{12}H_7N_3O_4$: C, 56.0; H, 2.7; N, 16.3. Found: C, 56.3; H, 2.8; N, 16.3.

4-(2-Phenyl-1,2,3-triazol-4-yl)butano-1,4-lactone 2,3-bis(arylhydrazones) (**12** *or* **13**). — A solution of compound **10** (1 mmol) in methanol (10 mL) was treated with the respective arylhydrazine (2 mmol), and the mixture was boiled under reflux for 10 min. The product that separated out on cooling was filtered off, washed with alcohol, and dried. It was recrystallized from ethanol to give red needles (see Table I).

Hydroxy-[1-phenyl-4-(phenylhydrazono)-2-pyrazolin-5-one-3-yl]-(2-phenyl-1,2,3-triazol-4-yl)methane (**16**). — A suspension of compound **12** (0.1 g) in water (50 mL) was heated with 2M sodium hydroxide solution (25 mL) for 30 min at 70–80°, whereupon the osazone completely dissolved. The pH of the resulting solution was adjusted to 6 with glacial acetic acid, and the product that separated out was filtered off, washed repeatedly with water and then ethanol, and dried (yield 60%). It was recrystallized from ethanol, to give orange needles; m.p. 79°; ν_{max}^{Nujol} 3400 (OH) and 1660 cm^{-1} (OCN).

Anal. Calc. for $C_{24}H_{19}N_7O_2$: C, 65.9; H, 4.4; N, 22.4. Found: C, 66.1; H, 4.3; N, 22.5.

Acetoxy-[1-phenyl-4-(phenylhydrazono)-2-pyrazolin-5-one-3-yl]-(2-phenyl-1,2,3-triazol-4-yl)methane (**17**). — A solution of compound **16** (0.2 g) in dry pyridine

TABLE I

MICROANALYTICAL AND SPECTRAL DATA FOR 4-(2-PHENYL-1,2,3-TRIAZOL-4-YL)BUTANO-1,4-LACTONE 2,3-BIS(ARYLHYDRAZONES) (**12** AND **13**)

Compound no.	*R*	*Yield (%)*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)*			*Found (%)*			ν^{Nujol}_{max} *(cm⁻¹)*	
					C	*H*	*N*	*C*	*H*	*N*		
12	H	75	250	$C_{24}H_{19}N_7O_2$	65.9	4.4	22.4	65.8	4.5	22.5	3250	1715
13	NO_2	88	115	$C_{24}H_{17}N_9O_6$	54.6	3.2	23.9	54.8	3.2	24.0	3220	1720

(3 mL) was treated with acetic anhydride (5 mL), and kept overnight at room temperature. The mixture was poured onto crushed ice, and the product that separated out was filtered off, washed repeatedly with water, and dried (yield 77%). It was recrystallized from ethanol–ether, to give yellow-orange needles; m.p. 220°; ν_{max}^{Nujol} 1730 (OAc) and 1660 cm^{-1} (OCN).

Anal. Calc. for $C_{26}H_{21}N_7O_3$: C, 65.1; H, 4.4; N, 20.4. Found: C, 65.2; H, 4.2; N, 20.5.

[1-Phenyl-4-(phenylhydrazono)-2-pyrazolin-5-one-3-yl]-(2-phenyl-1,2,3-triazol-4-yl)methane (**15**). — A solution of compound **6** (0.5 g) in 40% acetic acid (50 mL) was boiled under reflux for 1 h. An excess of phenylhydrazine (3 mL) was added, and boiling was continued for 90 min. The mixture was cooled, and the product that separated out after 24 h was filtered off, washed with ethanol, and recrystallized from ethanol, to give orange needles; m.p. 162°; ν_{max}^{Nujol} 1665 cm^{-1} (OCN).

Anal. Calc. for $C_{24}H_{19}N_7O$: C, 68.4; H, 4.5; N, 23.3. Found: C, 68.5; H, 4.5; N, 23.5.

1-Hydroxy-2-(phenylhydrazono)-1-(2-phenyl-1,2,3-triazol-4-yl)-2-(2-quinoxalinone-3-yl)ethane (**19**). — A solution of compound **10** (0.3 g) in methanol (10 mL) was treated with a solution of *o*-phenylenediamine (0.4 g) and phenylhydrazine (0.1 g) in methanol (10 mL), and the mixture was boiled on a hot-water bath for 10 min. The mixture was then cooled, and kept for 24 h at room temperature; the hydrazone that separated out was filtered off, washed with alcohol, and dried (yield 65%). Recrystallization was effected from ethanol, to give red needles; m.p. 225°; ν_{max}^{Nujol} 3350 (OH) and 1660 cm^{-1} (OCN).

Anal. Calc. for $C_{24}H_{19}N_7O_2$: C, 65.9; H, 4.4; N, 22.4. Found: C, 66.2; H, 4.2; N, 22.3.

Hydroxy-(1-phenylflavazol-3-yl)-(2-phenyl-1,2,3-triazol-4-yl)methane (**20**). — A suspension of compound **19** (0.5 g) in 0.01M sodium hydroxide solution (50 mL) and 1-butanol (2 mL) was boiled under reflux for 1 h. The yellow product resulting was filtered off, washed with water, dried (yield 70%), and recrystallized from ethanol; m.p. 198°; ν_{max}^{Nujol} 3300 cm^{-1} (OH).

Anal. Calc. for $C_{24}H_{17}N_7O \cdot H_2O$: C, 65.9; H, 4.4; N, 22.4. Found: C, 65.7; H, 4.4; N, 22.0.

Acetoxy-(1-phenylflavazol-3-yl)-(2-phenyl-1,2,3-triazol-4-yl)methane (**21**). — A solution of compound **20** (0.1 g) in dry pyridine (3 mL) was treated with acetic anhydride (2 mL), and the mixture was kept overnight at room temperature. It was poured onto crushed ice, and the acetate that separated out was filtered off, washed with water, and recrystallized from chloroform–ethanol, to give orange needles; m.p. 145°; ν_{max}^{Nujol} 1720 cm^{-1} (OAc).

Anal. Calc. for $C_{26}H_{21}N_7O_3$: C, 65.1; H, 4.4; N, 20.4. Found: C, 64.9; H, 4.2; N, 20.4.

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