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TRANSFORMATION OF THE HYDRAZONES OF 6-CHLORO-3-(L-*threo*-2,3,4-TRIHYDROXY-1-OXOBUTYL)-2-QUINOXALINONE INTO OTHER HETEROCYCLIC COMPOUNDS*

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ABSTRACT

The difference in reactivity of the two amino groups in 4-chloro-*o*-phenylenediamine allowed it to react with L-*threo*-2,3-hexodiulosono-1,4-lactone to give, after further reaction with various hydrazines, 6-chloro-3-(1-substituted-hydrazono-L-*threo*-2,3,4-trihydroxybutyl)-2-quinoxalinones (**5–14**), whose structures were deduced from their reactions, as well as from mass spectrometry of the (*p*-nitrophenyl)-hydrazone. Elimination of one mole of water per mole from these hydrazones gave the 1-aryl-6-chloro-3-(L-*threo*-glycerol-1-yl)flavazoles; the mass spectrum of one of these flavazoles is discussed. Elimination of two moles of water per mole from the hydrazones (**5**, **7**, and **8**) occurred with simulteneous cyclization to give 3-[1-aryl-5-(hydroxymethyl)pyrazol-3-yl]-6-chloro-2-quinoxalinones, whose acetylation gave the corresponding monoacetyl derivatives (that could also be obtained by the action of boiling acetic anhydride on the starting hydrazones). Periodate oxidation of the hydrazones and the flavazole derivatives afforded the corresponding aldehydes (that could react with hydrazines).

INTRODUCTION

Condensation of *o*-phenylenediamine with dehydro-L-ascorbic acid (**1**) should afford various products[1–7], depending upon possible reactions with the three reactive centers in **1**. When equimolar amounts of the reactants are used, two products[1–3] may be formed, according to whether the diamine reacts with the 1 and 2 carbonyl groups of **1** to give 3-(L-*threo*-2,3,4-trihydroxy-1-oxobutyl)-2-quinoxalinone, or with the 2 and 3 carbonyl groups to give 3-(L-*threo*-glycerol-1-yl)quinoxaline-2-carboxylic acid γ-lactone. In previous reports[8–10] in this series, we described the reaction of the former compound with a variety of aryl- and aroyl-hydrazines; the products were found to undergo a number of transformations leading to different types of heterocycles[8–11].

*Heterocycles from Carbohydrate Precursors. Part XI. For Part X, see E. S. H. El Ashry, I. E. El Kholy, and Y. El Kilany, *Carbohydr. Res.*, 67 (1978) 495–499.

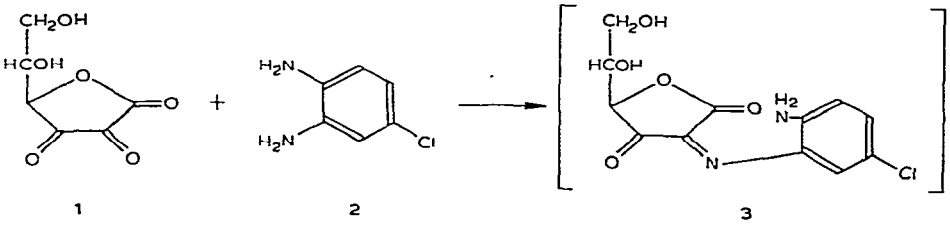
We now report the reaction of dehydro-L-ascorbic acid (**1**) with 4-chloro-*o*-phenylenediamine (**2**), followed by reaction of the product with aryl- and aroyl-hydrazines, and transformation of the resulting compounds into other heterocyclic derivatives. In addition to the synthetic interest of this study, it provides products that are potentially important as models for mass-spectrometric studies[8,12–16] of oligosaccharide sequences[12–15].

DISCUSSION

Although the interaction of equimolar quantities of *o*-phenylenediamine and dehydro-L-ascorbic acid might be anticipated to afford two possible products[1–3], depending on whether the reaction occurred on C-1 and C-2 or C-2 and C-3 of **1**, the situation would, when using a substituted diamine, be more complicated, because of the possibility of formation of two isomers of each of these feasible products. The formation of both isomers in each case would be expected to depend upon the difference in reactivity of the two amino groups, which would lead to a tendency for the more reactive amino group to undergo reaction with the more reactive carbonyl group in dehydro-L-ascorbic acid, followed by reaction of the second amino group with one of the two other carbonyl groups .The effect of the chlorine atom in **2** may arise from interplay between the inductive effect and a weak, resonance effect[17], which decreases the basicity of the amino group on C-1: consequently, that on C-2 of **2** is more basic, *i.e.* more reactive, and reacts first, with the 2-carbonyl group in **1**. In the next stage, the Schiff base (**3**), formed as an intermediate, cyclizes through C-1 of the residue of **1**, to give **4**, and this is followed by the reaction of C-1 of the side chain with the aryl- or aroyl-hydrazine.

This is what actually happened when **1** was allowed to react with **2**, followed by reaction of the product with various arylhydrazines, whereby red compounds were formed that were formulated as 3-(1-arylhydrazono-L-*threo*-2,3,4-trihydroxybutyl)-6-chloro-2-quinoxalinones (**5–10**), because the characteristic, red color[3,8] for this class of compounds indicated the involvement of C-1 and C-2 of **1**, and only a single product was isolated in each instance, indicating the formation of one isomer; however, no attempt was made to ascertain the constituents of the mother liquors. The phenylhydrazone derivative was reported[3] in a review by Henseke, but no details were given.

When, instead of arylhydrazines, aroylhydrazines were used, yellow products (**11–14**) were formed. The infrared spectra of compounds **5–14** showed the presence of bands at 1670–1640 cm^{-1} (due to the OCN groups) and at 3400 cm^{-1} (due to the OH groups). These derivatives were formulated as structures **5–14**, having acyclic side-chains, similar to the products previously obtained[8–10] by using *o*-phenylenediamine, on the basis of their reactions as well as their spectral data. The n.m.r. spectrum of **12** showed a two-proton multiplet, at δ 4.5, for a methylene group, a one-proton multiplet at δ 4.9 (H-3), and a one-proton doublet at δ 6.4 (H-2). A three-proton singlet appeared at δ 2.16 due to the methyl group of the *p*-tolyl group,



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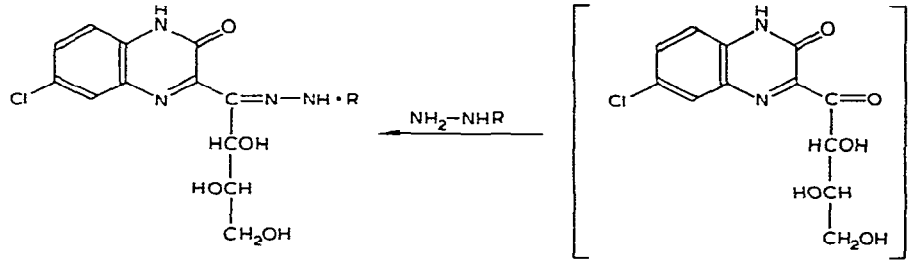


4

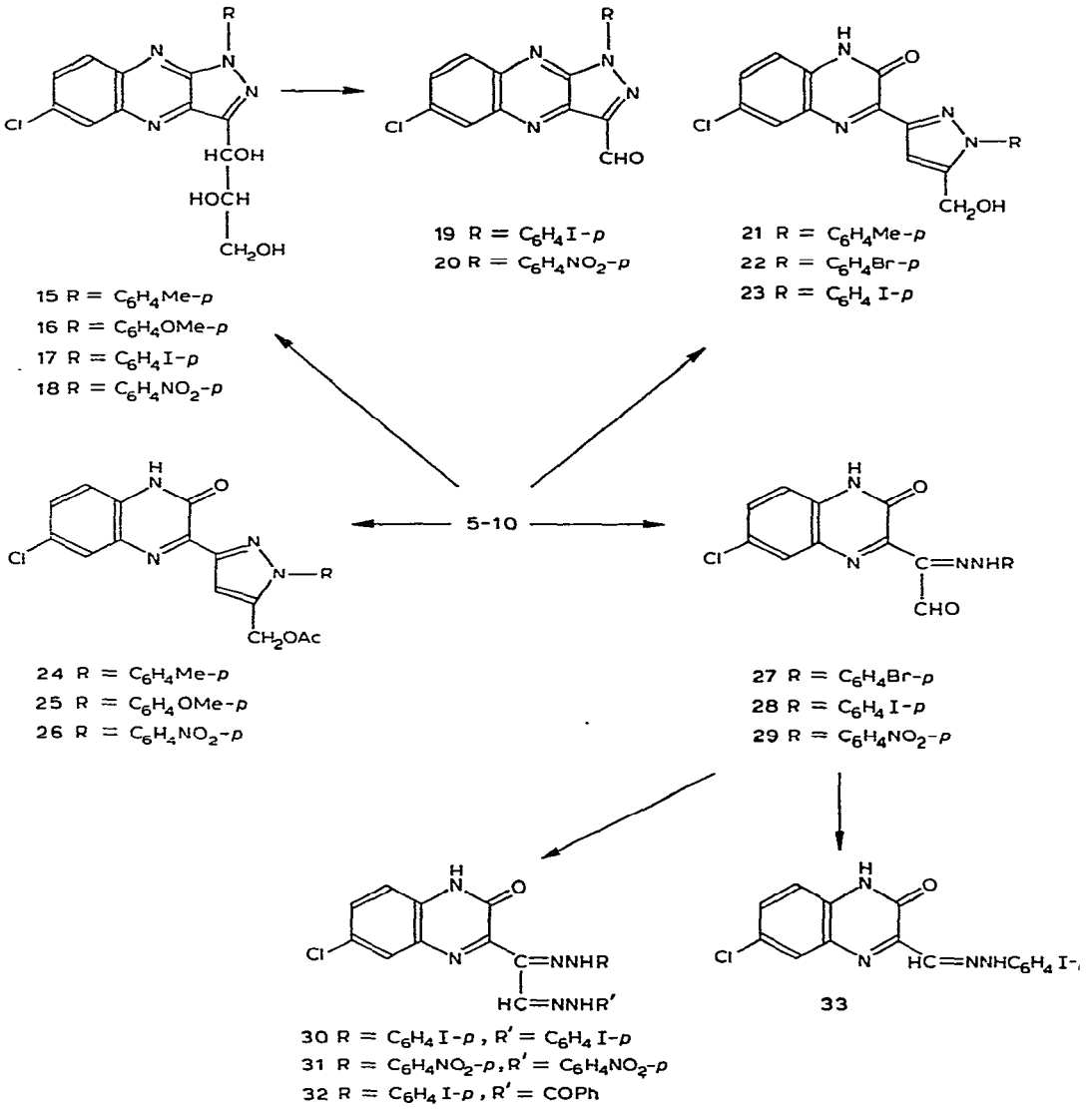
5 R = C_6H_4Me-*p*
6 R = C_6H_4OMe-*p*
7 R = C_6H_4Br-*p*
8 R = C_6H_4I-*p*
9 R = $C_6H_4NO_2$-*p*
10 R = $C_6H_4SO_2NH_2$-*p*
11 R = COPh
12 R = COC_6H_4Me-*p*
13 R = COC_6H_4Cl-*p*
14 R = COC_6H_4I-*p*

and the aromatic protons as a multiplet centered at δ 7.6. The mass spectrum of 6-chloro-3-[L-*threo*-2,3,4-trihydroxy-1-(*p*-nitrophenyl)hydrazonobutyl]-2-quinoxalinone (**9**) showed the presence of a pair of peaks due to the molecular ion at *m/e* 433 and 435. This was followed by a series of ions resulting from the loss of H_2O and $2H_2O$, as well as successive fragmentation of the trihydroxypropyl side-chain, which confirmed the structure assigned.

Whereas the action of alkali on the acetyl derivatives of **5–8** resulted in a deacetylative rearrangement into pyrazolylquinoxalinones, discussed later, the parent (unacetylated) derivatives afforded the pyrazoloquinoxalines (flavazoles) **15–18**; one molecule of water was eliminated per molecule, with cyclization of the hydrazone residue with C-2 of the quinoxalinone ring (instead of cyclization with the hydroxyalkyl side-chain to give the pyrazolylquinoxalinones that occurred with the acetates). The presence of the hydroxyalkyl group was confirmed, not only by the spectral data, but also by periodate oxidation of **17** and **18**, which resulted in the consumption of two moles of the oxidant per mole, with separation of the aldehydes

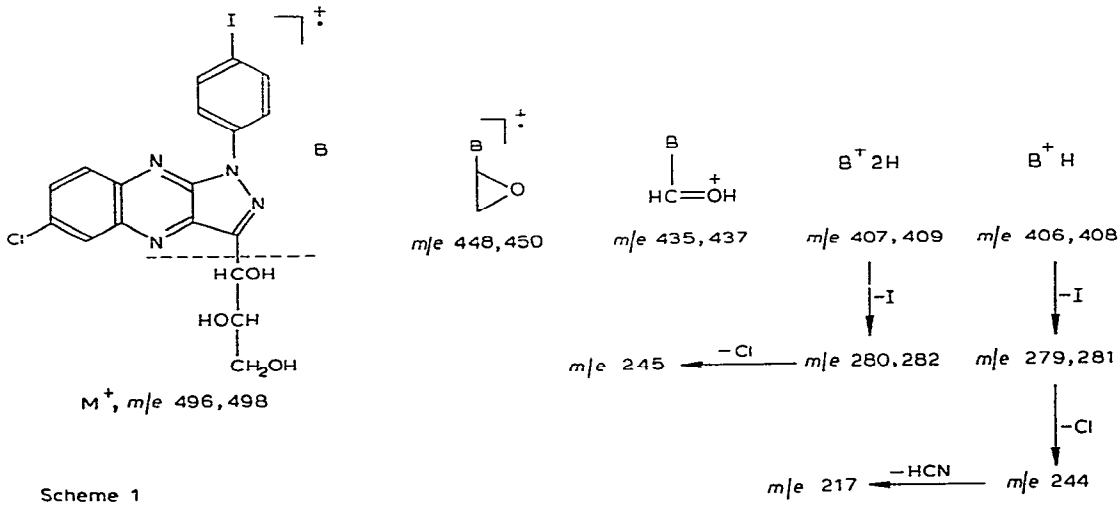
19 and **20**, respectively. These aldehydes are characterized by showing an i.r. band at 1700 cm^{-1} due to the aldehydic group, which does not appear in the i.r. spectra of their precursors.

The mass spectra of some 1-phenylflavazole derivatives of monosaccharides were reported by Dolejs and co-workers[15], who found structurally characteristic, mass-spectral fragmentation processes, in addition to the possible localization of a deoxy or methoxyl group in the sugar moiety. The mass spectra of the corresponding acetates were also reported[12–15], and their use in distinguishing between the inter-glucose bonds in oligosaccharides was investigated. In a previous report[8] in this series,



we discussed the mass spectra of 1-substituted phenylflavazoles; homologies within the spectra showed that similar bond-cleavage had taken place in such types of compounds. In the present work, we investigated the mass spectrum of 6-chloro-3-(L-*threo*-glycerol-1-yl)-1-(*p*-iodophenyl)flavazole (**17**); this agreed well with those studied in previous investigations[15,16]. It showed a molecular-ion peak at *m/e* 496, 498, and the base peak at *m/e* 435, 437 was attributed[15] to a benzylic cleavage of the flavazole ring. Elimination processes involving the sugar moiety take place similarly to those for 1-arylflavazoles. Thus, loss of O, H_2O, CHOH, and CH_2OH (or their combinations) from the molecular-ion peak occurs, to give ions that could be represented as previously reported[8,15,16], and that are shown in Scheme 1. Loss of the sugar moiety was noted, accompanied by transfer of one hydrogen atom (or two) to the flavazole ring, and this was also observed in some further fragmentations. The latter ion undergoes further loss, of the iodine and then the chlorine, to give a pair of ions at *m/e* 280, 282 and an ion at *m/e* 245, respectively. Loss of HCN from these heterocycles was observed.

Acetylation of 3-(1-arylhydrazono-L-*threo*-2,3,4-trihydroxybutyl)-6-chloro-2-quinoxalinones (**5**, **6**, and **9**) with boiling acetic anhydride resulted in the elimination of two molecules of water per molecule and acetylation of the rest of the molecule, to give 3-[5-(acetoxymethyl)-1-arylpyrazol-3-yl]-6-chloro-2-quinoxalinones (**27–29**). The same derivatives were also prepared either by boiling the acetylated derivative of **5**, **6**, and **9** with acetic anhydride, or by acetylating their unacetylated parents with acetic anhydride in pyridine. The latter 3-[1-aryl-5-(hydroxymethyl)pyrazol-3-yl]-6-chloro-2-quinoxalinones (**21–23**) were also prepared by two methods: by boiling **5**, **7**, and **8** with hydroxylamine hydrochloride, which caused the loss of two molecules of water per molecule, or by deacetylating the triacetyl derivative of **6** with sodium hydroxide, which led to simultaneous deacetylation and cyclization, to give **21**. All these pyrazoles and their acetyl derivatives are colorless compounds; this distinguishes



Scheme 1

TABLE I

MASS-SPECTRAL DATA FOR COMPOUNDS **9** AND **17**

Compound	m/e *values of principal fragments (relative intensity, %)*
6-Chloro-3-[L-*threo*-2,3,4-trihydroxy-(1-*p*-nitrophenylhydrazono)butyl]-2-quinoxalinone (9)	433 (M), 415 (M − H_2O, 21), 397 (M − 2 H_2O, 73), 384 (M − H_2O − CH_2OH, 6), 372 (M − CH_2OH − CHOH, 13), 369 (M − 2 H_2O − CO, 50), 367 (M − 2 H_2O − CHOH, 36), 354 (372 − H_2O, 92), 343 (372 − CHO, 28), 339 (369 − CHOH, 11), 338 (369 − CH_2OH, 10), 326 (354 − CO, 7), 324 (354 − CHOH, 4), 308 (354 − NO_2, 13), 280 (326 − NO_2, 9), 279 (13), 220 (372 − CHOH − $C_6H_4NO_2$, 6), 206 (372 − CHOH − $NC_6H_4NO_2$, 60), 180 (206 − CN, 24), 179 (21), 165 (220 − N_2 − HCN, 28), 152 (180 − CO), 138 ($O_2NC_6H_4NH_2$, 93), 122 ($O_2NC_6H_4$, 32)
6-Chloro-3-(L-*threo*-glycerol-1-yl)-1-(*p*-iodophenyl)flavazole (17)	496 (M, 14), 480 (M − O, 1), 465 (M − H_2O − O, 2), 462 (M − CH_2OH, 3), 449 (M − CH_2OH − O, 2), 436 (B + 31, 68), 435 (B + 30, 100), 420 (B + 31 − O, 3), 419 (B + 31 − OH, 3), 407 (B + 2H, 12), 406 (B + H, 2), 392 (B − 13, 2), 380 (B + 1 − CN, 1), 309 (B + 31 − I, 6), 308 (B + 30 − I, 5), 280 (B + 2 − I, 15), 279 (B + 1 − I, 45), 253 (B + 1 − I − HCN, 14), 245 (B + 2 − I − Cl, 2), 244 (B + 1 − I − Cl, 6), 217 (B + 1 − I − Cl − HCN, 4), 203 (IC_6H_4, 4)

them from their parent precursors (which are red), and from the flavazoles (which are yellow, and formed by the loss of one molecule of water per molecule). The i.r. spectra of the pyrazolylquinoxalinones **21–23** and their acetates **24–26** showed a band at 1660 cm^{-1} (due to the OCN group), and a band at 1740–1720 cm^{-1} that appeared only in the spectra of the acetates (due to OAc). The mass spectrum of **25** showed a pair of peaks at *m/e* 424, 426 corresponding to the molecular ion, which is in complete agreement with the structures assigned. Periodate oxidation of **7–9** and **11** gave 3-(1-arylhydrazonoglyoxal-1-yl)-6-chloro-2-quinoxalinones (**27–29**); this confirmed the acyclic-side chain structures for **5–14**. Reaction of these aldehydes with aryl- or aroylhydrazines afforded the corresponding hydrazones (**30–32**).

In conclusion, the reactions outlined afford attractive compounds capable of various transformations into other heterocyclic compounds, indicating the generality of the reactions applied; they allow nuclear substitutions in the quinoxaline ring by the use of substituted diaminobenzenes.

EXPERIMENTAL

General methods. — Melting points were determined with a Kofler-block apparatus and are uncorrected. I.r. spectra were recorded with a Unicam SP200 spectrometer, and n.m.r. spectra (for solutions in pyridine-d_5) with a Jeol-100

spectrometer, with tetramethylsilane as the standard. Chemical shifts are given on the δ scale. Mass spectra were recorded with an A.E.I. MS902 instrument. Microanalyses were performed in the Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt.

*3-(1-Arylhydrazono-*L-threo-*2,3,4-trihydroxybutyl)-6-chloro-2-quinoxalinones* (**5–10**). — (*a*) A mixture of L-ascorbic acid (0.01 mole) and benzoquinone (0.01 mole) in methanol (15 mL) was stirred for 1 h, and then treated with a solution of 4-chloro-*o*-phenylenediamine (0.01 mole) in methanol (15 mL) and water (50 mL). The mixture was boiled under reflux for 4 min, the arylhydrazine (0.01 mole) was then added, and the mixture was refluxed for a further 5 min. The products that separated were filtered off, washed successively with ethanol and ether, and dried. They were recrystallized from ethanol, to give red needles (see Table II).

(*b*) A suspension of L-ascorbic acid (0.01 mole) in water (50 mL) and methanol (25 mL) was treated with 4-chloro-*o*-phenylenediamine (0.01 mole), the arylhydrazine (0.02 mole), and acetic acid (1.5 mL). The mixture was boiled under reflux for 1 h, whereby red, crystalline products separated out that were identical with the products obtained by method (*a*).

*3-(1-Aroylhydrazono-*L-threo-*2,3,4-trihydroxybutyl)-6-chloro-2-quinoxalinones* (**11–14**). — These compounds were prepared as for the preparation of **5–10** by method *a*, but using aroylhydrazines instead of arylhydrazines (see Table III).

*1-Aryl-6-chloro-3-(*L-threo-*glycerol-1-yl)flavazoles* (**15–18**). — A suspension of each of compounds **5–9** (3 mmoles) in 0.01M sodium hydroxide (60 mL) was refluxed with a mixture of butanol (6 mL) and methanol (3 mL) for 1 h. The mixture was then cooled, and filtered; the solid was washed with water, and the yellow product was recrystallized from ethanol (see Table IV).

1-Aryl-6-chloro-3-formylflavazoles (**19**, **20**). — A suspension of compound **17** or **18** (0.2 g) in distilled water was stirred with the calculated amount of sodium metaperiodate for 24 h. The mixture was filtered, and the solid was washed with water, and recrystallized from ethanol (see Table IV).

3-[1-Aryl-5-(hydroxymethyl)pyrazol-3-yl]-6-chloro-2-quinoxalinones (**21–23**). — (*a*) A solution of compound **5**, **7**, or **8** (2 mmoles) and hydroxylamine hydrochloride (0.02 mole) in methanol (15 mL) was refluxed for 6 h. The mixture was cooled, and diluted with water, and the product that separated was filtered off, and washed with cold methanol (see Table V).

(*b*) A solution of the acetate of compound **5** (1 mmole) in ethanol (15 mL) was treated with 1M sodium hydroxide (15 mL), and the mixture was heated under reflux for 4 h, cooled, acidified with acetic acid, and the solid product recrystallized from ethanol, to give colorless needles, identical with those obtained by method (*a*).

3-[5-(Acetoxymethyl)-1-arylpyrazol-3-yl]-6-chloro-2-quinoxalinones (**24–26**). — A solution of compound **5**, **6**, or **9** (2 mmoles) in acetic anhydride (5–10 mL) was boiled under reflux for 15 min, and the mixture was cooled, and poured onto crushed ice. The product was recrystallized from ethanol, to give colorless needles (see Table VI).

TABLE II

MICROANALYTICAL AND SPECTRAL DATA FOR 3-(1-ARYLHYDRAZONO-L-*threo*-2,3,4-TRIHYDROXYBUTYL)-6-CHLORO-2-QUINOXALINONES

Compound No.	*R*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)*			*Found (%)*			ν_{max}^{Nujol} (cm^{-1})	
				C	*H*	*N*	*C*	*H*	*N*		
5	C_6H_4Me-*p*	210	$C_{19}H_{19}ClN_4O_4$	56.7	4.8	13.9	56.7	5.2	13.5	3400	1663
6	C_6H_4OMe-*p*	195	$C_{19}H_{19}ClN_4O_5$	54.5	4.6	13.4	54.8	4.8	13.8	3350	1665
7	C_6H_4Br-*p*	225	$C_{18}H_{16}BrClN_4O_4$	46.2	3.5	12.0	46.1	3.7	12.0	3400	1660
8	C_6H_4I-*p*	210–212	$C_{18}H_{16}ClIN_4O_4$	42.0	3.1	10.9	42.2	3.3	10.5	3450	1660
9	$C_6H_4NO_2$-*p*	250	$C_{18}H_{16}ClN_5O_6$	49.8	3.7	16.2	49.5	4.3	15.8	3410	1655
10	$C_6H_4SO_2NH_2$-*p*	241	$C_{18}H_{18}ClN_5O_6S$	46.2	3.9	15.0	46.3	4.0	15.0	3525	1667

TABLE III

MICROANALYTICAL AND SPECTRAL DATA FOR 3-(1-AROYLHYDRAZONO-L-*threo*-2,3,4-TRIHYDROXYBUTYL)-6-CHLORO-2-QUINOXALINONES

Compound No.	*R*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)*			*Found (%)*			ν_{max}^{Nujol} (cm^{-1})	
				C	*H*	*N*	*C*	*H*	*N*		
11	COPh	150	$C_{19}H_{17}ClN_4O_5$	54.8	4.1	13.4	54.9	4.1	13.4	3450	1670
12	COC_6H_4Me-*p*	172	$C_{20}H_{19}ClN_4O_5$	55.8	4.4	13.0	55.6	4.7	12.8	3400	1670
13	COC_6H_4Cl-*p*	152–155	$C_{19}H_{16}Cl_2N_4O_5$	50.6	3.6	12.4	51.1	3.5	11.9	3400	1660
14	COC_6H_4I-*p*	160	$C_{19}H_{16}ClIN_4O_5$	42.1	3.0	10.3	41.8	3.1	10.2	3400	1675

TABLE IV

MICROANALYTICAL AND SPECTRAL DATA FOR 1-ARYL-6-CHLORO-3-(L-*threo*-GLYCEROL-1-YL)FLAVAZOLES AND THEIR DERIVATIVES

Compound No.	*R*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)*			*Found (%)*			ν_{max}^{Nujol} (cm^{-1})	
				C	*H*	*N*	*C*	*H*	*N*		
15	C_6H_4Me-*p*	213–214	$C_{19}H_{17}ClN_4O_3$	59.3	4.5	14.6	58.9	4.5	14.7	3400	
16	C_6H_4OMe-*p*	137–140	$C_{19}H_{17}ClN_4O_4$	56.9	4.3	14.0	56.9	3.7	13.9	3400	
17	C_6H_4I-*p*	210	$C_{18}H_{14}ClIN_4O_3$	43.5	2.8	11.3	43.8	3.1	11.4	3320	
18	$C_6H_4NO_2$-*p*	230	$C_{18}H_{14}ClN_5O_5$	52.0	3.4	16.8	51.9	3.6	17.2	3400	
19	C_6H_4I-*p*	297–300	$C_{16}H_8ClIN_4O$	44.2	1.9	12.9	44.3	2.1	13.3		1700
20	$C_6H_4NO_2$-*p*	>300	$C_{16}H_8ClN_5O_3$	54.3	2.3	19.8	54.3	2.7	20.2		1700

TABLE V

MICROANALYTICAL AND SPECTRAL DATA FOR 3-[1-ARYL-5-(HYDROXYMETHYL)PYRAZOL-3-YL]-6-CHLORO-2-QUINOXALINONES

Compound No.	*R*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)*			*Found (%)*			ν_{max}^{Nujol} (cm^{-1})	
				C	*H*	*N*	*C*	*H*	*N*		
21	C_6H_4Me-*p*	323–325	$C_{19}H_{15}ClN_4O_2$	62.2	4.1	15.3	62.1	4.1	15.3	3400	1660
22	C_6H_4Br-*p*	320–322	$C_{18}H_{12}BrClN_4O_2$	50.1	2.8	13.0	50.1	2.7	13.4	3400	1660
23	C_6H_4I-*p*	310–312	$C_{18}H_{12}ClIN_4O_2$	45.2	2.5	11.7	45.5	2.4	11.7	3400	1660

TABLE VI

MICROANALYTICAL AND SPECTRAL DATA FOR 3-[5-(ACETOXYMETHYL)-1-ARYLPYRAZOL-3-YL]-6-CHLORO-2-QUINOXALINONES

Compound No.	*R*	*M.p. (degrees)*	*Molecular formula*	*Calculated* (%)			*Found* (%)			ν_{max}^{Nujol} (cm^{-1})		
				C	*H*	*N*	*C*	*H*	*N*			
24	C_6H_4Me-*p*	248	$C_{21}H_{17}ClN_4O_3$	61.7	4.2	13.7	61.6	4.2	13.5	3400	1740	1660
25	C_6H_4OMe-*p*	279	$C_{21}H_{17}ClN_4O_4$	59.4	4.0	13.2	59.7	4.3	13.6	3350	1735	1680
26	$C_6H_4NO_2$-*p*	302–303	$C_{20}H_{14}ClN_5O_5$	54.6	3.2	15.9	54.5	3.3	15.5	3250	1720	1680

TABLE VII

MICROANALYTICAL AND SPECTRAL DATA FOR 6-CHLORO-3-(1-SUBSTITUTED-HYDRAZONO-GLYOXAL-1-YL)-2-QUINOXALINONES

Compound No.	*R*	*M.p. (degrees)*	*Molecular formula*	*Calculated* (%)			*Found* (%)			ν_{max}^{Nujol} (cm^{-1})
				C	*H*	*N*	*C*	*H*	*N*	
27	C_6H_4Br-*p*	281	$C_{16}H_{10}BrClN_4O_2$	47.4	2.5	13.8	47.8	2.8	13.5	1660
28	C_6H_4I-*p*	280	$C_{16}H_{10}ClIN_4O_2$	42.5	2.2	12.4	42.6	2.5	12.4	1655
29	COPh	>300	$C_{17}H_{11}ClN_4O_3$	57.6	3.1	15.8	57.6	3.2	15.6	1662

TABLE VIII

MICROANALYTICAL AND SPECTRAL DATA FOR 3-(1,2-BIS(ARYLHYDRAZONO)GLYOXAL-1-YL)-6-CHLORO-2-QUINOXALINONES AND MIXED AROYL–ARYL DERIVATIVES

Compound No.	*R*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)*			*Found (%)*			ν_{max}^{Nujol} (cm^{-1})
				C	*H*	*N*	*C*	*H*	*N*	
30	C_6H_4I-*p* R′ = C_6H_4I-*p*	260	$C_{22}H_{15}Cl_2N_6O$	39.5	2.3	12.6	39.8	2.5	13.0	1678
31	$C_6H_4NO_2$-*p* R′ = $C_6H_4NO_2$-*p*	>300	$C_{22}H_{15}ClN_8O_5$	52.1	3.0	22.0	52.4	3.0	22.1	1660
32	C_6H_4I-*p* R′ = COPh	289–290	$C_{23}H_{16}ClIN_6O_2$	48.4	2.8	14.7	48.5	3.1	14.7	1655

3-(1-Substituted-hydrazono-glyoxal-1-yl)-6-chloro-2-quinoxalinones (**27–29**). — A stirred mixture of each of compounds **7** to **9** (0.01 mole) and sodium metaperiodate (0.03 mole) in distilled water (10 mL) was kept overnight at room temperature. The title compounds that separated out were filtered off, washed with water, dried, and recrystallized from butanol, to give orange-red needles (see Table VII).

3-[1,2-Bis(arylhydrazono)glyoxal-1-yl]-6-chloro-2-quinoxalinones (**30, 31**). — A solution of compound **28** or **29** (1 mmole) in 1-butanol (60 mL) was boiled under reflux with the arylhydrazine (1.2 mmoles) and a few drops of acetic acid for 5 min. The product that separated out was filtered off, washed with ethanol, and dried (see Table VIII).

3-(2-Aroylhydrazono-1-arylhydrazono-glyoxal-1-yl)-6-chloro-2-quinoalinone (**32**). — A solution of compound **28** (1 mmole) in 1-butanol (60 mL) was similarly treated with the aroylhydrazine, and processed as in the previous experiment (see Table VIII).

6-Chloro-2-quinoxalinone-3-carboxaldehyde p-*iodophenylhydrazone* (**33**). — A suspension of compound **28** (0.4 g) in methanol (17 mL) was treated with 0.01M sodium hydroxide (33 mL), and the mixture was boiled under reflux for 60 h. The product was filtered off, successively washed with water and ethanol, and dried. It was recrystallized from 1-butanol; m.p. >300°; ν_{max}^{Nujol} 3475 (NH) and 1660 cm^{-1} (OCN).

Anal. Calc. for $C_{15}H_{10}ClIN_4O$: C, 42.4; H, 2.4; N, 13.2. Found: C, 42.8; H, 2.3; N, 12.8.

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