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SYNTHESIS OF SOME PYRAZOLE DERIVATIVES HAVING L-*threo* AND D-*erythro* SIDE CHAINS*

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ABSTRACT

The mixed bis(arylhydrazones) of L-*threo*-2,3-hexodiulosono-1,4-lactone rearrange into pyrazolediones. Mono- and bis-(arylhydrazones) of isoascorbic acid were prepared; the latter are present in two forms that afford the same pyrazoledione. Acetylation, benzoylation, and periodate oxidation of these pyrazolediones were studied, and some condensation products from the pyrazole aldehyde were prepared. Some of the i.r. and mass-spectral data were discussed.

INTRODUCTION

There has been an increasing interest in the synthesis of heterocyclic *C*-glycosyl compounds as a consequence of the biological activity of the natural *C*-nucleosides[1,2]. One of the indirect approaches for the synthesis of such nucleosides is the use of acyclic *C*-nucleosides having sugar moieties capable of forming furanoid rings[3–6]; this primarily requires the availability of methods for the synthesis of various heterocycles having sugar moieties attached. Some of the 4,5-pyrazolediones and their derivatives were evaluated[7–14] as potential drugs for the central nervous system, and as antidiabetic, antidiuretic, anthelmintic, antiviral, and anticancer agents. These various biological activities suggested for such compounds attracted our attention to the synthesis of some pyrazolediones having varied substituents on the ring and a carbohydrate moiety on C-3. Bis(arylhydrazones) are useful precursors for the synthesis of heterocycles[15,16]; consequently, some mixed bis(arylhydrazones) of L-*threo*-2,3-hexodiulosono-1,4-lactone, as well as bis(arylhydrazones) of the D-*erythro* analog (isoascorbic acid), were prepared, and converted into the corresponding pyrazolediones. The successful application of such reactions to those of the mixed type allowed the synthesis of substituted heterocycles having two different aryl substituents.

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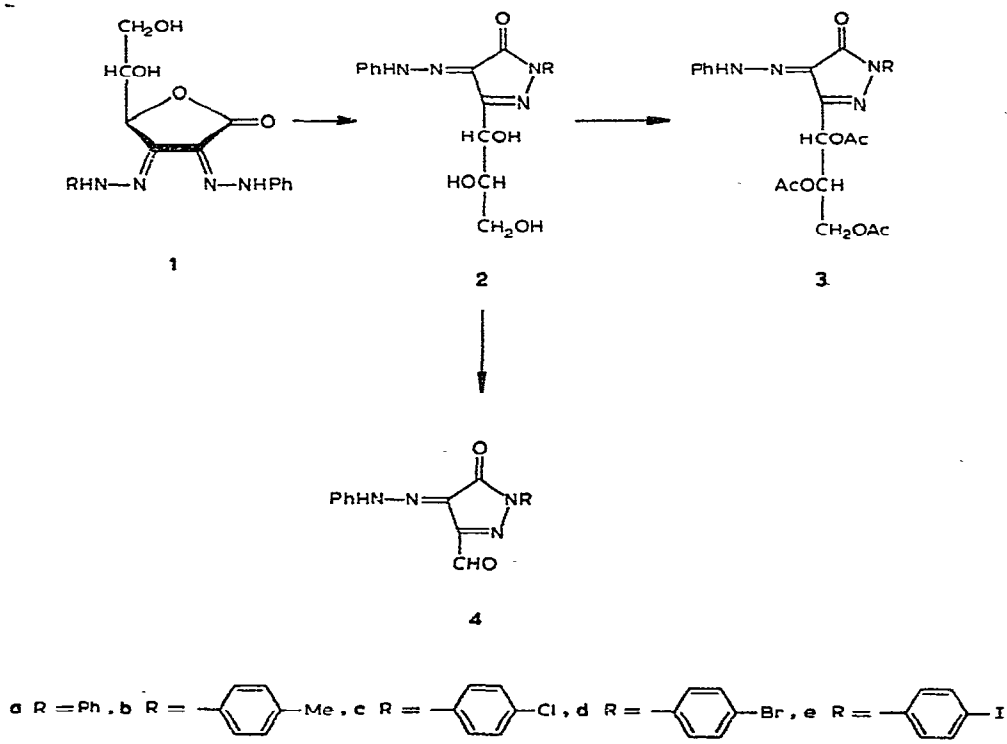
DISCUSSION

The bis(arylhydrazones) of L-*threo*-2,3-hexodiulosono-1,4-lactone were reported[17,18] to undergo conversion into the corresponding 1-aryl-3-(L-*threo*-glycerol-1-yl)-4,5-pyrazoledione 4-(2-arylhydrazones) by the action of alkali followed by acidification. In the present study, we were interested in the preparation of pyrazoles having different aryl substituents. To achieve this requirement, bis(arylhydrazones) of the mixed type (**1b–e**) of L-*threo*-2,3-hexodiulosono-1,4-lactone were used as starting materials. When these mixed bishydrazones were subjected to rearrangement under alkaline conditions, followed by acidification, they afforded 3-(L-*threo*-glycerol-1-yl)-4,5-pyrazoledione 4-(2-phenylhydrazone) compounds (**2b–e**) having varied substituents on N-1, such as *p*-tolyl, *p*-chlorophenyl, *p*-bromophenyl, and *p*-iodophenyl. These compounds **2b–e** (see Scheme 1) were characterized by their orange



Scheme 1

color, which differs from that of the starting bishydrazones (red). They have characteristic infrared spectra showing an amide band in the carbonyl region at 1665–1660 cm^{-1}, in contrast to the lactone band at 1725–1720 cm^{-1} for the starting bishydrazones;

the hydroxyl absorption appears at 3400–3300 cm^{-1}. Acetylation of the pyrazoles 2d and 2e with acetic anhydride in pyridine afforded the *O*-acetyl derivatives 3d and 3e, having in their infrared spectra bands at 1740 cm^{-1} due to the *O*-acetyl groups, in addition to the amide band at 1660 cm^{-1} present in the spectra of their parent compounds, whereas the hydroxyl absorption shown by the latter had disappeared.

The mass spectrum of 1-(*p*-bromophenyl)-3-(1,2,3-tri-*O*-acetyl-L-*threo*-glycerol-1-yl)-4,5-pyrazoledione 4-(2-phenylhydrazone) (3d) showed the molecular-ion peak

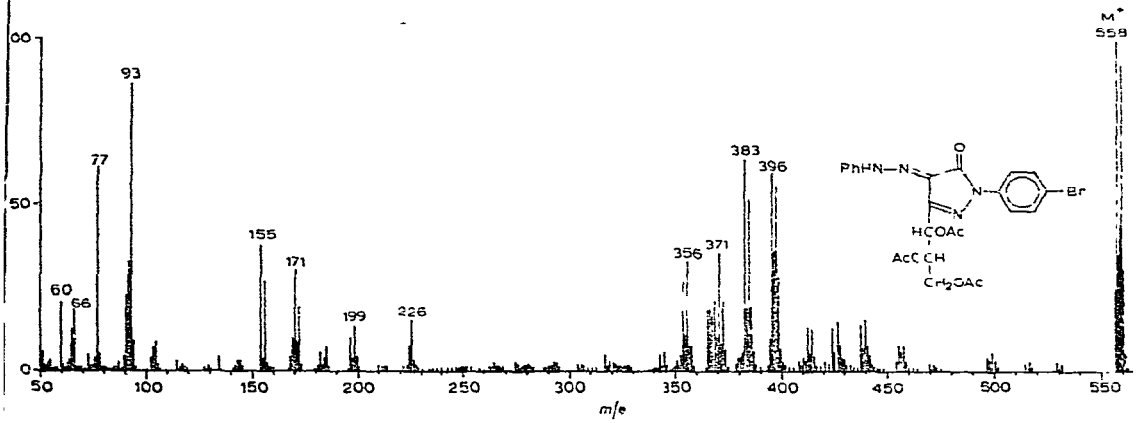


Fig. 1. The mass spectrum of 1-(*p*-bromophenyl)-3-(1,2,3-tri-*O*-acetyl-L-*threo*-glycerol-1-yl)-4,5-pyrazoledione 4-(2-phenylhydrazone) (3d).

at *m/e* 558,560, which is the base peak; it appears as two peaks having almost the same intensity due to the equal abundance of the two isotopes of bromine. This was followed by three main series of ions, which could be designated as C-3, C-2, and C-1 according to the number of the carbon atom (of the sugar moiety) present in the fragment. The ions belonging to the C-3 series start by splitting of an *O*-acetyl group (in the form of acetic acid) from the molecular ion, giving rise to a pair of peaks corresponding to $(M-60)^+$ at *m/e* 498,500. After this splitting, there is a series of consecutive eliminations of the remaining *O*-acetyl groups, characterized by 1,2-elimination of acetic acid and of ketene from the *O*-acetyl group attached to the double-bonded carbon atom[19–21]. Thus, ion $(M-60)^+$ fragments in this way, giving peaks at *m/e* 438,440, 456,458 and 396,398 represented by the ions C-3b–d. The C-2 series is represented by fragments of relatively low abundance which started by rupture of the C-2–C-3 bond and elimination of the C-1 acetate group to give the C-2a ion at *m/e* 425,427. This was followed by elimination of ketene from the *O*-acetyl group attached to the double bond (as in the previous fragmentation) to give a pair of peaks corresponding to the C-2b ion at *m/e* 383,385. Then, the aldehydic group was eliminated, giving rise to the C-1a ion at *m/e* 354,356. The C-2b ion undergoes loss of the N-1 substituent, giving the C-2c ion at *m/e* 226 and the *p*-bromophenylinium

ion at *m/e* 155 and 157. More-intense peaks, corresponding to the ions of the C-1 series, arise by rupture of the C-1–C-2 bond followed by loss of ketene, to give ions at *m/e* 413,415 and 371,373. The ions representing the C-2 series are usually started by loss of a proton from the hydrazone of the R residue. These fragmentation patterns of the sugar part (see Scheme 2) are similar to that reported for *N*-phenylosotriazoles[22]. These series of ions are followed at lower *m/e* value by a group of fragments belonging to the *p*-bromophenyl group in the region *m/e* 155–199, and then by a group belonging to the phenyl group in the region *m/e* 77–119, as shown in Table I, indicating that both aryl groups are involved in the fragmentation.

TABLE I

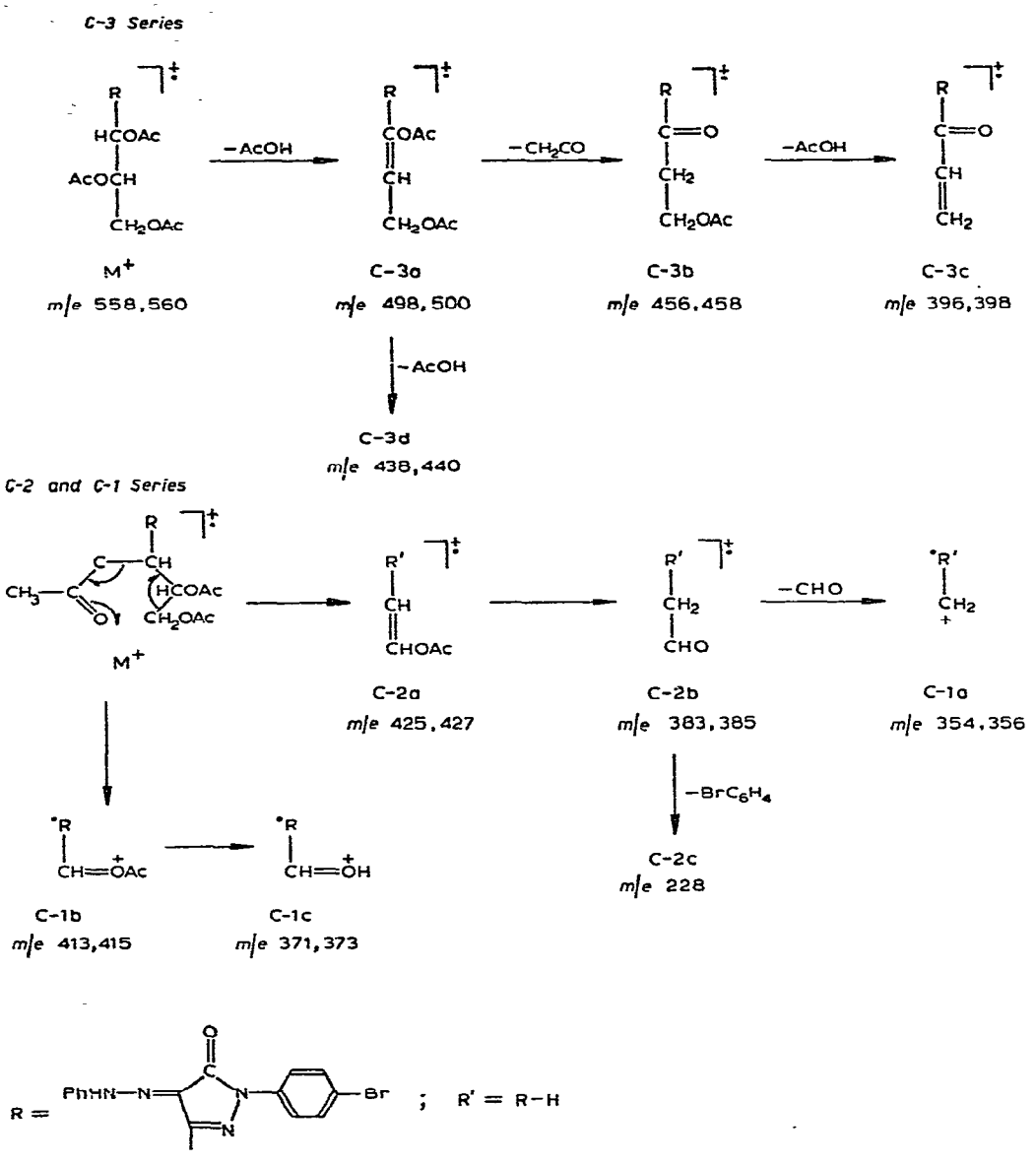
MASS-SPECTRAL FRAGMENTATION OF THE ARYL SUBSTITUENTS

m/e	*ion*	m/e	*ion*
119	$PhNCO^+$	197, 199	$BrC_6H_4NCO^+$
105	$PhNN^+$	183, 185	$BrC_6H_4NN^+$
93	$PhNH_2^+$	171, 173	$BrC_6H_4NH_4^+$
77	Ph^+	155, 157	$BrC_6H_4^+$

Periodate oxidation of 1 mole of 3-(L-*threo*-glycerol-1-yl)-1-*p*-tolyl-4,5-pyrazoledione 4-(2-phenylhydrazone) (**2b**) resulted in the consumption of two moles of oxidant, and the separation of 3-formyl-1-*p*-tolyl-4,5-pyrazoledione 4-(2-phenylhydrazone) (**4**). The i.r. spectrum of **4** showed a band at 1695 cm^{-1} due to the aldehyde group, in addition to the amide band at 1655 cm^{-1}, and there was no hydroxyl absorption.

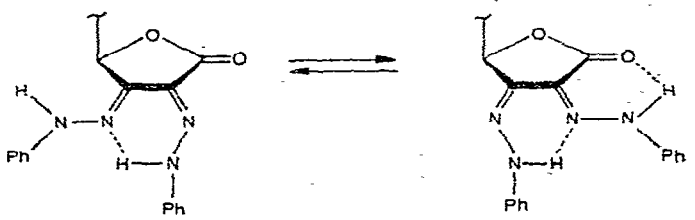
The reaction of the oxidized form of isoascorbic acid (D-*erythro*-2,3-hexodiulosono-1,4-lactone) (**5**) with phenylhydrazine was reported[23] to give the mono- or the bis-(phenylhydrazone) according to the reaction conditions. In the present work, the reaction of **5** was extended to substituted phenylhydrazines. Thus, when **5** reacted with one molecular equivalent of the respective substituted arylhydrazine at room temperature, it afforded the corresponding mono(arylhydrazone), namely, the 2-[2-(*p*-chlorophenyl)-, 2-[2-(*p*-bromophenyl)-, and 2-[2-(*p*-iodophenyl)-hydrazones] (**6c–e**) of D-*erythro*-2,3-hexodiulosono-1,4-lactone. The position of the hydrazone group on C-2 was proved by treating the compounds with alkali, followed by acidification and then reaction with an arylhydrazine, whereby no pyrazole derivatives (expected from compounds having their hydrazone groups on C-3) were observed. The i.r. spectrum of compounds **6** showed two bands in the carbonyl region, one at 1750 cm^{-1} due to the lactone group, and the other, at 1675 cm^{-1}, due to the carbonyl group involving C-3.

Reaction of the mono(arylhydrazones) (**6**) with arylhydrazines gave the corresponding bis(arylhydrazones) (**8**); these were also prepared by the direct reaction of **5** with arylhydrazines, including *p*-chloro-, *p*-bromo-, and *p*-iodo-phenylhydrazine.



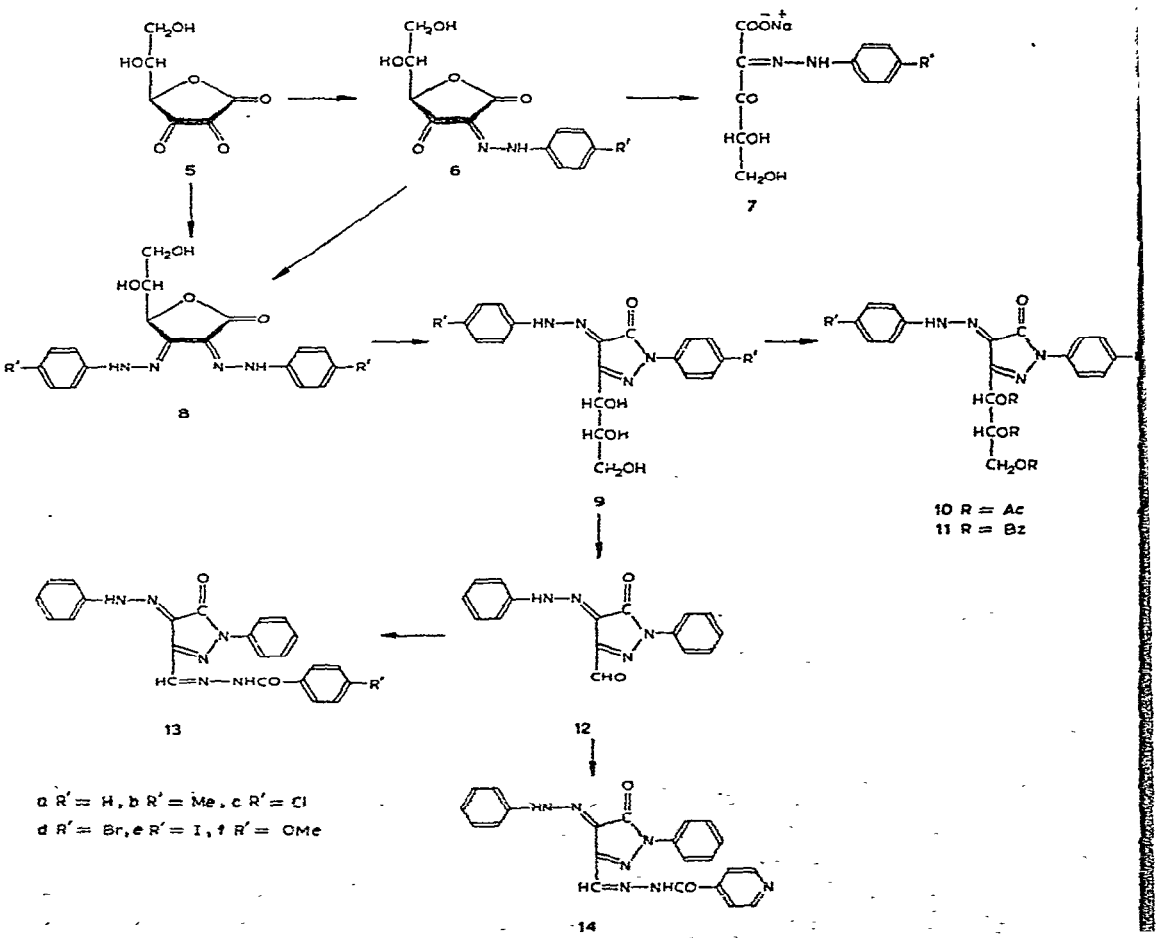
Scheme 2

whereby products separated during the heating period. These bis(arylhydrazones) (8) crystallized in two forms that were interchangeable by recrystallization. The two forms differ in their color; one is orange, and the other, red. The orange forms showed a carbonyl lactone band in their i.r. spectra, at higher frequency than for the red forms. This phenomenon was reported[23] for the bis(phenylhydrazone)



Type 1 Type 2

Scheme 3



a R′ = H, b R′ = Me, c R′ = Cl
d R′ = Br, e R′ = I, f R′ = OMe

10 R = Ac
11 R = Bz

derivative, and, on the basis of n.m.r. study, was attributed[23] to a structural transformation involving the change of a chelate system of type 1 into a hydrogen-bonded system of type 2 (see Scheme 3).

When these bis(arylhydrazones) (8) were heated with sodium hydroxide, and the solution then acidified with acetic acid. they rearranged to 1-aryl-3-(D-*erythro*-glycerol-1-yl)-4,5-pyrazoledione 4-(2-arylhydrazones) (9). Either of the types of the bishydrazones 8 (type 1 or 2) afforded the same pyrazole. In this way, pyrazoles having *p*-tolyl, *p*-chlorophenyl, *p*-bromophenyl, and *p*-iodophenyl as the substituent were prepared. Acetylation of the 4-(2-arylhydrazones) (9) with acetic anhydride in pyridine gave 1-aryl-3-(1,2,3-tri-*O*-acetyl-D-*erythro*-glycerol-1-yl)-4,5-pyrazoledione 4-(2-arylhydrazones) (10). Similarly, benzoylation of 9 with benzoyl chloride in pyridine afforded the tri-*O*-benzoyl derivatives 11. Compounds 10 and 11 showed in their infrared spectra the absorption of the carbonyl amide of the heterocyclic ring at 1670–1660 cm^{-1}; 10 showed a band at 1750–1740 cm^{-1} due to the OAc, and 11 at 1725–1720 cm^{-1} due to the OBz.

The pyrazoledione derivatives 9 consumed two moles of periodate per mole, with the separation of the same aldehyde as that obtained from the corresponding L-*threo* analog. 3-Formyl-1-phenyl-4,5-pyrazoledione 4-(2-phenylhydrazone) (12) was condensed with a number of aroylhydrazines, yielding crystalline derivatives 13 and 14. Thus, it gave an orange benzoylhydrazone, *p*-toluoylhydrazone, (*p*-methoxybenzoyl)hydrazone, (*p*-chlorobenzoyl)hydrazone, and isonicotinoylhydrazone. Their i.r. spectra showed one, unresolved band, at 1680 cm^{-1}, due to the two amides in the case of the benzoylhydrazone derivative, whereas the other hydrazones showed two bands, one at 1695–1670 cm^{-1} due to the carbonyl amide of the hydrazone residue, and the other at 1660 cm^{-1} due to the carbonyl amide of the heterocyclic ring.

EXPERIMENTAL

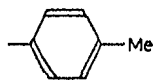
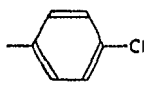
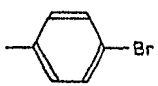
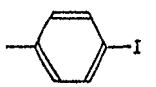
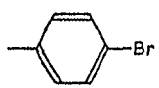
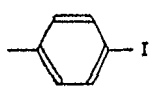
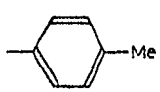
General methods. — Melting points were determined with a Kofler block apparatus and are uncorrected. I.r. spectra were recorded with a Unicam SP-200 spectrometer. Microanalyses were performed in the Chemistry Department, Faculty of Science, Cairo University Cairo, Egypt.

1-Aryl-3-(L-threo-*glycerol-1-yl*)*-4,5-pyrazoledione 4-(2-phenylhydrazones)* (2). — A suspension of the bishydrazone 1 (1 g) in water (50 ml) was heated with 2M sodium hydroxide (25 ml) at 70–80° until the bishydrazone had dissolved. The pH was then brought to 7 with acetic acid and the product was filtered off, washed several times with water, and recrystallized from ethanol to give orange needles (see Table II).

*1-Aryl-3-(1,2,3-tri-*O*-acetyl-*L-threo-*glycerol-1-yl)-4,5-pyrazoledione 4-(2-phenylhydrazones)* (3). — A suspension of 2 (0.5 g) in dry pyridine (10 ml) was treated with acetic anhydride (4 ml) and kept overnight at room temperature. The mixture was poured onto crushed ice, and the acetate that separated was filtered off, and crystallized from chloroform–ethanol in yellow-orange needles (see Table II).

TABLE II

MICROANALYTICAL AND SPECTRAL DATA FOR 1-ARYL-3-(L-*threo*-GLYCEROL-1-YL)-4,5-PYRAZOLEDIONE 4-(2-PHENYLHYDRAZONES) AND THEIR DERIVATIVES

Compound No.	*R*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)*				*Found (%)*				ν_{max}^{Nujol}	
				C	*H*	*Hal*	*N*	*C*	*H*	*Hal*	*N*		
2b		209–211	$C_{19}H_{20}N_4O_4$	62.0	5.5		15.2	61.6	5.5		14.9	1660	3300
2c		208–209	$C_{18}H_{17}ClN_4O_4$	55.6	4.4		14.4	55.9	4.6		14.8	1660	3350
2d		190–192	$C_{18}H_{17}BrN_4O_4$	49.9	4.0	18.4	13.4	50.4	4.1	18.7	13.9	1665	3400
2e		205–206	$C_{18}H_{17}IN_4O_4$	45.0	3.6	26.5	11.7	45.3	4.0	27.0	10.0	1660	3400
3d		164–165	$C_{24}H_{23}BrN_4O_7$	51.5	4.1	14.3	10.0	51.1	4.2	14.8	9.6	1660	1740
3e		148–149	$C_{24}H_{23}IN_4O_7$	47.5	3.8		9.2	47.1	3.9		9.6	1660	1740
4b		161–163	$C_{17}H_{14}N_4O_2$	66.7	4.6		18.3	66.3	4.8		18.6	1655	1695

Mass spectral data for compound **3d**. *m/e* 562 (5), 561 (31), 560 (95), 559 (36), 558 (100), 532 (2), 530 (2), 528 (1), 527 (2), 525 (2), 500 (2), 499 (6), 498 (4), 497 (4), 473 (1), 472 (2), 470 (2), 459 (2), 458 (8), 457 (6), 456 (8), 455 (4), 442 (4), 441 (8), 440 (16), 439 (7), 438 (13), 428 (8), 427 (16), 426 (5), 425 (13), 416 (4), 415 (13), 414 (5), 413 (13), 412 (1), 411 (2), 409 (2), 400 (6), 399 (29), 398 (57), 397 (37), 396 (61), 395 (10), 387 (6), 386 (19), 385 (53), 384 (19), 383 (66), 382 (6), 381 (4), 380 (4), 379 (2), 374 (6), 373 (22), 372 (7), 371 (36), 370 (11), 369 (22), 368 (17), 367 (20), 366 (19), 359 (1), 358 (7), 357 (8), 356 (30), 355 (11), 354 (28), 353 (4), 352 (1), 351 (2), 346 (1), 345 (6), 344 (1), 343 (5), 328 (1), 327 (1), 326 (1), 322 (1), 321 (2), 319 (2), 317 (5), 306 (2), 304 (2), 294 (2), 293 (2), 292 (1), 282 (1), 281 (2), 280 (1), 279 (1), 276 (2), 275 (4), 227 (4), 226 (16), 225 (7), 200 (5), 199 (16), 198 (4), 197 (11), 186 (7), 185 (5), 184 (2), 183 (6), 182 (2), 174 (1), 173 (20), 172 (10), 171 (31), 170 (10), 169 (4), 158 (2), 157 (28), 156 (4), 155 (40), 145 (4), 144 (4), 135 (5), 119 (2), 118 (2), 117 (1), 115 (4), 106 (2), 105 (8), 104 (7), 103 (5), 94 (10), 93 (89), 92 (35), 91 (23), 90 (5), 87 (4), 86 (1), 78 (6), 77 (62), 76 (4), 75 (1), 73 (5), 66 (18), 65 (12), 64 (4), 63 (2), 60 (22), 55 (4), 54 (2), 53 (1), and 51 (6).

1-Aryl-3-formyl-4,5-pyrazoledione 4-(2-phenylhydrazones) (**4**). — A solution of compound **2** (1 g) in ethanol was treated with a solution of sodium metaperiodate (1 g) in water (10 ml), and kept for 30 min at room temperature. The mixture was diluted with water, and the product was filtered off after another 30 min, washed with water, and dried. It crystallized from ethanol in yellow-orange needles (see Table II).

D-erythro-*2,3-Hexodiulosono-1,4-lactone 2-(2-arylhydrazones)* (**6**). — A solution of compound **5** (0.01 mole) in water (50 ml) was treated with the arylhydrazine (0.01 mole) in ethanol (10 ml). The mixture was kept overnight at room temperature, whereby a yellow crystalline product separated out. It was filtered off, and recrystallized from ethanol (see Table III).

Action of alkali on **6**. — A suspension of compound **6** (0.1 g) in water (5 ml) was heated with 2M sodium hydroxide (5 ml) until dissolution occurred. The solution was then cooled, made neutral with acetic acid, and the product treated with the corresponding arylhydrazine to give **8**.

D-erythro-*2,3-Hexodiulosono-1,4-lactone 2,3-bis(2-arylhydrazones)* (**8**). — (*a*) A hot solution of compound **6** (1 mmole) in ethanol was treated with the arylhydrazine (1 mmole). The mixture was heated under reflux for 10 min, and cooled, whereby the bis(arylhydrazone) separated out. Each was recrystallized from ethanol (see Table IV).

(*b*) A solution of **5** (0.01 mole) in water (50 ml) was treated with the arylhydrazine (0.02 mole). The mixture was heated on a boiling water bath for 1 h, whereby the red bis(arylhydrazone) separated out. Each was recrystallized from ethanol; each was identical with that obtained by procedure (*a*).

1-Aryl-3-(D-erythro-*glycerol-1-yl)-4,5-pyrazoledione 4-(2-arylhydrazones)* (**9**).— These compounds were prepared from **8** as for the preparation of **2** (see Table V).

*1-Aryl-3-(1,2,3-tri-*O*-acetyl-*D-erythro-*glycerol-1-yl)-4,5-pyrazoledione 4-(2-arylhydrazones)* (**10**). — A solution of compound **9** (0.5 g) in dry pyridine (10 ml) was treated with acetic anhydride (5 ml), and kept overnight at room temperature. The

TABLE III

MICROANALYTICAL AND SPECTRAL DATA FOR D-*erythro*-2,3-HEXODIULOSONO-1,4-LACTONE 2-(2-ARYLHYDRAZONES)

Compound No.	*R'*	*M.p. (degrees)*	*Molecular formula*	*Calculated* (%)			*Found* (%)			ν_{max}^{Nujol}		
				C	*H*	*N*	*C*	*H*	*N*			
6c	Cl	198–199	$C_{12}H_{11}ClN_2O_5$	48.3	3.7	9.4	48.7	4.0	9.2	1675	1750	3400
6d	Br	213–214	$C_{12}H_{11}BrN_2O_5$	42.0	3.2	8.2	42.4	3.5	7.8	1675	1750	3500
6e	I	227–228	$C_{12}H_{11}IN_2O_5$	36.9	2.8	7.2	36.5	2.6	7.6	1680	1750	3400

TABLE IV

MICROANALYTICAL AND SPECTRAL DATA FOR D-*erythro*-2,3-HEXODIULOSONO-1,4-LACTONE 2,3-BIS(2-ARYLHYDRAZONES)

Compound No.	*Color*	*R'*	*M.p. (degrees)*	*Molecular formula*	*Calculated* (%)			*Found* (%)			ν_{max}^{Nujol}	
					C	*H*	*N*	*C*	*H*	*N*		
8c	orange	Cl	206–207	$C_{18}H_{16}Cl_2N_4O_4$	51.1	3.8	13.2	51.1	3.6	13.2	1750	3450
8d	red	Br	220–221	$C_{18}H_{16}Br_2N_4O_4$	42.2	3.2	10.9	41.9	3.5	10.5	1725	3400
8e	red	I	215–216	$C_{18}H_{16}I_2N_4O_4$	35.7	2.7		35.4	2.7		1720	3400

TABLE V

MICROANALYTICAL AND SPECTRAL DATA FOR 1-ARYL-3-(D-*erythro*-GLYCEROL-1-YL)-4,5-PYRAZOLEDIONE 4-(2-ARYLHYDRAZONES) AND THEIR ACYLATED DERIVATIVES

Compound No.	*R'*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)*			*Found (%)*			ν_{max}^{Nujol}	
				C	*H*	*N*	*C*	*H*	*N*		
9b	Me	217–218	$C_{20}H_{22}N_4O_4$	62.8	5.8	14.7	62.5	5.6	15.0	1660	3400
9c	Cl	227–228	$C_{18}H_{16}Cl_2N_4O_4$	51.1	3.8	13.2	50.8	3.6	12.9	1660	3420
9d	Br	219–220	$C_{18}H_{16}Br_2N_4O_4$	42.2	3.2	10.9	42.6	2.9	10.6	1660	3450
10c	Cl	186–187	$C_{24}H_{22}Cl_2N_4O_7$	52.5	4.0	10.2	52.7	3.9	10.7	1670	1740
10d	Br	170–171	$C_{24}H_{22}Br_2N_4O_7$	45.2	3.6	8.8	44.9	4.0	9.1	1665	1750
11c	Cl	204–205	$C_{39}H_{28}Cl_2N_4O_7$	63.7	3.8	7.6	63.9	4.2	7.9	1660	1720
11d	Br	172–173	$C_{39}H_{28}Br_2N_4O_7$	56.8	3.4	6.8	57.1	3.6	6.9	1660	1720

TABLE VI

MICROANALYTICAL AND SPECTRAL DATA FOR 3-(AROYLHYDRAZONES) OF 3-FORMYL-1-PHENYL-4,5-PYRAZOLEDIONE 4-(2-PHENYLHYDRAZONE)

Compound No.	*R'*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)*			*Found (%)*			ν_{max}^{Nujol}	
				C	*H*	*N*	*C*	*H*	*N*		
13a	H	245–247	$C_{23}H_{18}N_6O_2 \cdot H_2O$	64.5	4.7	19.6	64.2	5.0	20.0	1680	
13b	Me	158–160	$C_{24}H_{20}N_6O_2 \cdot H_2O$	65.1	5.0	19.0	64.9	5.2	19.2	1680	1660(sh)
13f	OMe	157–160	$C_{24}H_{20}N_6O_3 \cdot H_2O$	62.9	4.8	18.3	63.0	4.8	18.5	1675	1660(sh)
13c	Cl	167–169	$C_{23}H_{17}ClN_6O_2 \cdot H_2O$	59.7	4.1	18.2	59.3	4.5	18.3	1680	1660
14		188–190	$C_{22}H_{17}N_7O_2 \cdot H_2O$	61.5	4.5	22.8	61.5	4.4	22.7	1695	1660

mixture was poured onto crushed ice, and the acetate that separated was filtered off, and washed repeatedly with water. The acetate was recrystallized from chloroform–ethanol (see Table V).

1-Aryl-3-(1,2,3-tri-O-benzoyl-D-erythro-glycerol-1-yl)-4,5-pyrazoledione 4-(2-arylhydrazones) (**11**). — A solution of compound **9** (0.5 g) in dry pyridine (10 ml) was treated with benzoyl chloride (2 ml), and kept overnight at room temperature. The mixture was poured onto crushed ice, and the benzoate that separated was filtered off, and washed repeatedly with water. The benzoate was recrystallized from chloroform–ethanol, giving red needles (see Table V).

3-Formyl-1-phenyl-4,5-pyrazoledione 4-(2-phenylhydrazone) (**12**). — A solution of compound **9a** in ethanol was treated with a solution of sodium metaperiodate, and the mixture was processed as for **4a**; the product was recrystallized from ethanol, to give **12**, m.p. 138–140° (lit.[18] m.p. 139–141°).

3-(Aroylhydrazones) of 3-formyl-1-phenyl-4,5-pyrazoledione 4-(2-phenylhydrazone) (**13** *and* **14**). — A solution of **12** (0.1 g) in ethanol (20 ml) was heated under reflux for 30 min with the respective aroylhydrazine. Each product crystallized from ethanol in orange crystals (see Table VI).

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