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STUDIES ON DEHYDRO-L-ASCORBIC ACID 2-ARYLHYDRAZONE 3-OXIMES: CONVERSION INTO SUBSTITUTED TRIAZOLES AND ISOXAZOLINES+

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The 2-*o*-bromo and 2-*o*-chlorophenyltriazoles of dehydro-L-ascorbic acid (*L-threo*-2,3-hexodiulosono-1,4-lactone) were prepared through dehydrative cyclization of the corresponding 2-arylhydrazone 3-oximes. Upon treatment with liquid ammonia, the triazole 3 afforded the triazole carboxamides 4, characterized as the tri- and tetra-acetates. Reaction of 2 with bromine in water, caused its cyclization to the triazole 7. Controlled reaction of 2 with alkali followed by neutralization, gave the isoxazolines 8. Reaction of 2 with HBr-HOAc, gave the bromodeoxy derivatives 10, these were converted into the corresponding triazoles 11 on treatment with acetic anhydride-pyridine.

Key words: Ascorbic acid, Hydrazones.

INTRODUCTION

Many of the reactions of dehydro-*L*-ascorbic acid bishydrazones (*L-threo*-2,3-hexodiulosono-1,4-lactone 2,3-bishydrazones) differ from those of the sugar osazones (glycosulose 1,2-bishydrazones). The former readily undergo cyclizations involving either nucleophilic attack of a hydrazone nitrogen atom on the 1-carbonyl group, or attack of a hydroxy group on the hydrazone residue. Thus, for example, oxidation of dehydro-*L*-ascorbic acid bishydrazones, yields bicyclic azo compounds [1,2] whereas the glycosulose osazones yield triazoles [3]. The insecticidal properties [4] of 2-m-chloro and 2-p-chlorophenyl sugar triazoles have attracted the attention to the synthesis of the 2-*o*-chlorophenyl derivatives. The 2-m- and p-chlorophenyltriazoles [5,6] were prepared by oxidizing the corresponding bishydrazones with heavy metal salts such as copper sulfate. And by applying this reaction on bis(*o*-chlorophenylhydrazone), the phenyltriazole was obtained as a hydrogen atom replaced the chlorine atom. In the present work, the 2-*o*-bromo- and 2-*o*-chlorophenyl triazole of dehydro-L-ascorbic acid were prepared for the first time through dehydrative cyclization of the corresponding 2-arylhydrazone 3-oximes.

EXPERIMENTAL

General methods. — Melting points were determined with Tottoli (Buchi) apparatus and are uncorrected. I.R. spectra were recorded with a 580B Perkin-Elmer spectrometer, and n.m.r. spectra (for solutions in chloroform-d), with tetramethylsilane as the standard with a Varian EM-390 spectrometer. Chemical shifts are given on the scale. Mass spectra were recorded with M60 spectrometer. Microanalyses were performed in the Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt.

L-threo-2,3-hexodiulosono-1,4-lactone 2-arylhydrazone (2). . . . A solution of *L-threo*-2,3-hexodiulosono-1,4-lactone (1; 0.1 mol) in water (80 mL) was treated with the desired arylhydrazone (0.1 mol) in ethanol (20 mL) The mixture was kept overnight at room temperature, the monoarylhydrazone that separated was filtered off, washed with water and dried. Recrystallization from ethanol gave compounds 2 as yellow needles. Melting points, formulas, analyses, and i.r. data are listed in Table 1.

L-threo-2,3-Hexodiulosono-1,4-lactone 2-arylhydrazone 3-oximes (3). . . . A solution of the monoarylhydrazone 2 (1 g) in ethanol (50 mL) was treated with hydroxylamine hydrochloride (1.5 g) and sodium acetate (1.5 g), and the mixture was boiled under reflux for 6 hr. It was concentrated, and the solid that separated out was filtered off, washed with water, and dried. Each compound was recrystallized from ethanol, giving yellow needles. (Table 1).

2-Aryl-4-(2,3-di-O-acetyl-L-threo-glycerol-l-yl)-1,2,3-triazole-5-carboxylic acid lactone (4). - - - (a) A suspension of compound 3 (0.1 g) in acetic anhydride (10 mL) was boiled under reflux for 1 h. The mixture was poured onto crushed ice, and the product was filtered off, washed with water, and dried. The products were recrystallized from ethanol, giving colorless needles (Table 2).

+Triazole Derivatives from Dehydroascorbic acids, Part VI. For Part V, see ref. 8.

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(b) A suspension of compound 3 (0.1 g) in dry pyridine (5 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 was filtered off, and recrystallized from ethanol, to give colorless needles identical with those obtained from method (a).

2-Aryl-4-(L-threo-glycerol-l-yl)-1,2,3-triazole 5-carboxamides (5).- - - A solution of compound 4 (1 g) in methanol (20 mL) was treated with concerntrated ammonia (10 mL) and kept overnight at room temperature. The solution was concentrated under diminished pressure to a small volume and the solid that separated was filtered off, and dried. The products were recrystallized from ethanol in cololess needles (Table 2).

2-Aryl-4-(1,2,3-tri-O-acetyl-L-threo-glycerol-1-yl)-1,2,3-triazole 5-carboxamides (6). - - - A solution of each compound 5 (0.1 g) in dry pyridine (5 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 was filtered off, washed with water and dried. The products were recrystallized from ethanol, giving colorless needles (Table 2).

Triazole tetraacetates (7).— A suspension of each compound 5 (0.1 g) in acetic anhydride (5 mL) was boiled under reflux for 1 h. The mixture was then cooled, and

Table 1. Microanalytical and IR data for compounds 2 and 3.

Compound	Ar	M.P. (degrees)	Molecular Formula		Analysis C	H	Hal.	N	KBr ν_{max} (cm^{-1})		
2a	C_6H_4Br-*o*	148-149	$C_{12}H_{11}BrN_2O_5$	Calc.	42.00	3.23	23.29	8.16	3450,	1720,	1680
				Found	42.24	3.51	23.50	8.22			
2b	C_6H_4Cl-*o*	163-164	$C_{12}H_{11}ClN_2O_5$	Calc.	48.25	3.72	11.87	9.37	3450,	1760,	1680
				Found	48.54	3.59	11.68	9.60			
3a	C_6H_4Br-*o*	238-239	$C_{12}H_{12}BrN_3O_5$	Calc.	40.24	3.38	22.31	11.73	3400,	1730	
				Found	40.50	3.40	22.53	11.62			
3b	C_6H_4Cl-*o*	224-225	$C_{12}H_{12}ClN_3O_5$	Calc.	45.94	3.85	11.30	13.38	3380,	1740	
				Found	46.0	3.71	11.65	13.51			

Table 2. Microanalytical and IR data for compounds 4-6.

Compound	Ar	M.P. (degrees)	Molecular Formula		Analysis C	H	Hal.	N	KBr ν_{max} (cm^{-1})	
4a	C_6H_4Br-*o*	105-106	$C_{16}H_{14}BrN_3O_6$	Calc.	45.30	3.33	18.83	9.90	1800,	1740
				Found	45.64	3.50	18.92	9.71		
4b	C_6H_4Cl-*o*	113-114	$C_{16}H_{14}ClN_3O_6$	Calc.	50.60	3.72	9.33	11.06	1800,	1740
				Found	50.76	3.92	9.50	11.36		
5a	C_6H_4Br-*o*	197-198	$C_{12}H_{13}BrN_4O_4$	Calc.	40.32	3.64		15.68	3450,	1680
				Found	40.48	3.82		15.40		
5b	C_6H_4Cl-*o*	144-146	$C_{12}H_{13}ClN_4O_4$	Calc.	46.09	4.19		17.91	3450,	1680
				Found	46.32	4.23		18.02		
6a	C_6H_4Br-*o*	153-154	$C_{18}H_{19}BrN_4O_7$	Calc.	44.73	3.96		11.60	1740,	1680
				Found	44.62	3.89		11.60		
6b	C_6H_4Cl-*o*	133-134	$C_{18}H_{19}ClN_4O_7$	Calc.	49.26	4.36	8.07		1740,	1680
				Found	49.59	4.62	8.42			

poured onto crushed ice, and the product that separated was filtered off, washed with water, and dried. Each product was recrystallized from ethanol in colorless needles. (Table 3).

2-Aryl-4-formyl-1,2,3-triazole 5-carboxamides (8).— A suspension of each compound 5 (0.1 g) in water (10 mL) was treated with a solution of sodium metaperiodate (0.3 g) and the mixture was shaken for 6 h. The solid that separated was filtered off, washed with water, and dreid. Each compound was recrystallized from ethanol, giving colorless needles (Table 3).

2-Aryl-4-(hydroxymethyl)-1,2,3-triazole 5-carboxamides (9).— A solution of each compound 8 (0.1 g) in methanol (10 mL) was treated with a solution of sodium borohydride (0.1 g) in water (10 mL), added in small portions with occasional shaking. The solution was acidified with

Table 3. Microanalytical and IR data for compounds 7-9.

Compound	Ar	M.P. (degrees)	Molecular Formula		Analysis C	H	Hal.	N	KBr νmax (cm^{-1})
7a	C_6H_4Br-*o*	139-140	$C_{20}H_{21}BrN_4O_8$	Calc.	45.73	4.03		10.66	1740, 1660
				Found	45.36	4.22		10.79	
7b	C_6H_4Cl-*o*	122-123	$C_{20}H_{21}ClN_4O_8$	Calc.	49.95	4.40	7.37	11.64	1740, 1660
				Found	50.23	4.51	7.70	11.97	
8a	C_6H_4Br-*o*	215-216	$C_{10}H_7BrN_4O_2$	Calc.	40.70	2.40		19.0	1700, 1660
				Found	40.72	2.63		19.43	
8b	C_6H_4Cl-*o*	203-205	$C_{10}H_7ClN_4O_2$	Calc.	47.92	2.81	14.14	22.34	1700, 1660
				Found	47.48	2.60	14.56	22.51	
9a	C_6H_4Br-*o*	199-200	$C_{10}H_9BrN_4O_2$	Calc.	40.42	3.06		18.90	3450, 1660
				Found	40.76	3.20		18.64	
9b	C_6H_4Cl-*o*	166-168	$C_{10}H_9ClN_4O_2$	Calc.	47.54	3.60		22.16	3450, 1660
				Found	47.70	4.0		22.40	

Table 4. Microanalytical and IR data for compounds 10-12.

Compound	Ar, Ar′	M.P. (degrees)	Molecular Formula		Analysis C	H	N	KBr νmax (cm^{-1})
10a	C_6H_4Br-*o*	148-149	$C_{12}H_{11}BrN_4O_3$	Calc.	42.50	3.37	16.51	1740, 1660
				Found	42.43	3.21	16.23	
10b	C_6H_4Cl-*o*	132-134	$C_{12}H_{11}ClN_4O_3$	Calc.	48.91	3.76	19.03	1740, 1660
				Found	48.72	3.52	19.36	
11a	C_6H_4Br-*o*	112-114	$C_{14}H_{13}BrN_4O_4$	Calc.	44.11	3.44		1740, 1660
				Found	44.36	3.58		
11b	C_6H_4Cl-*o*	120-121	$C_{14}H_{13}ClN_4O_4$	Calc.	49.94	3.90	16.63	1740, 1660
				Found	49.72	3.72	16.50	
12a	$C_6H_3Br_2$-*o,p*	187-188	$C_{12}H_9Br_2N_3O_4$	Calc.	34.38	2.16	10.02	3450, 1800
				Found	34.52	2.41	10.46	
12b	C_6H_3BrCl-*o,p*	165-167	$C_{12}H_9BrClN_3O_4$	Calc.	38.50	2.40	11.2	3450, 1800
				Found	38.6	2.3	11.5	

aceticacid, and the solid that separated was filtered off, washed with water, and dried. It was recrystallized from ethanol, to give colorless needles (Table 3).

4-Acetoxymethyl-2-aryl-1,2,3-trizole 5-carboxamides (10).— A solution of compound 9 (0.1 g) in dry pyridine (5 mL) was treated with acetic anhydride (5 mL) and kept overnight at room temperature. The mixture was poured onto crushed ice, and the product was filtered off, washed with water, and dried. It was recrystallized from ethanol in colorless needles (Table 4).

Triazole diacetates (11).— A solution of compound 9 (0.1 g) in acetic anhydride (5 mL) was boiled under reflux for 1 hr. The mixture was cooled, poured onto crushed ice, and the product was filtered off, washed with water, and dried. It was recrystallized from ethanol in colorless needles (Table 5).

2-Aryl-4-(L-threo-1,2,3-trihydroxypropyl)-1,2,3-triazole 5-carboxylic acid lactone (12).— A suspension of compound 3 (0.1 g) in water (10 mL) was treated portionwise with bromine (1 mL) in water (10 mL) with stirring. Stirring was continued for 12 hr at room temperature, and the excess bromine was removed by passing a stream of air. The product was filtered off, washed with water, and dried. It was recrystallized from ethanol in colorless prisms (Table 4).

5-0-Acetyl-6-bromo-6-deoxy-L-threo-2,3-hexodiulosone-1,4-lactone-2-(arylhydrazone)-3-oximes (14).— To each compound 3 (0.1 g) was added HBr-HOAc (10 mL), and the mixture was stirred for 24 h at room temperature. water (30 mL) was added, and the sold that separated was filtered off, washed with water, and dried. It was recrystallized from ethanol, to give yellow needles (Table 5).

2-Aryl-4-(L-threo-2-acetoxy-3-bromo-3-deoxy-l-hydroxypropyl)-1,2,3-triazole 5-carboxylic acid lactone (15).— A suspension of compound 14 (0.1 g) in acetic anhydride (5 mL) was boiled under reflux for 1 h. The mixture was

Table 5. Microanalytical and IR data for compounds 14-17.

Compound	Ar	M.P. (degrees)	Molecular Formula		Analysis C	H	N	KBr νmax (cm^{-1})
14a	C_6H_4Br-*o*	193-194	$C_{14}H_{13}Br_2N_3O_5$	Calc.	36.31	2.83	9.07	1740
				Found	36.64	2.6	9.36	
14b	C_6H_4Cl-*o*	211-213	$C_{14}H_{13}BrClN_3O_5$	Calc.	40.16	3.13	10.03	1740
				Found	40.49	3.42	10.36	
15a	C_6H_4Br-*o*	145-146	$C_{14}H_{11}Br_2N_3O_4$	Calc.	37.77	2.5	9.4	1800, 1740
				Found	37.4	2.61	9.53	
15b	C_6H_4Cl-*o*	102-104	$C_{14}H_{11}BrClN_3O_4$	Calc.	41.96	2.76	10.48	1800, 1740
				Found	42.09	2.54	10.63	
16a	C_6H_4Br-*o*	144-146	$C_{12}H_{12}BrN_3O_5$	Calc.	40.24	3.38	11.73	3350, 1730
				Found	40.58	3.40	11.96	
16b	C_6H_4Cl-*o*	150-152	$C_{12}H_{12}ClN_3O_5$	Calc.	45.94	3.85	13.38	3350, 1730
				Found	45.79	3.62	13.69	
17a	C_6H_4Br-*o*	99-100	$C_{18}H_{18}BrN_3O_8$	Calc.	44.64	3.74	8.67	1740
				Found	44.92	3.61	8.55	
18a	C_6H_4Br-*o*	224-224	$C_{18}H_{16}Br_2N_4O_4$	Calc.	42.21	3.15	10.93	3450, 1730
				Found	42.65	3.49	11.37	
18b	C_6H_4Cl-*o*	224-226	(Lit.[9] 226)					
19a	C_6H_4Br-*o*	173174	$C_{18}H_{14}Br_2N_4O_4$	Calc.	42.38	2.76	11.0	3450, 1740
				Found	42.54	2.93	10.73	
19b	C_6H_4Cl-*o*	164-166	(Lit.[9] 165-166)					

poured onto crushed ice, and the product was filtered off, washed with water, and dried. It was recrystallized from ethanol, giving colorless needles (Table 5).

3-(L-threo-glycerol-l-yl)-4,5-isoxazolinedione 4-(arylhydrazones) (16).--- A suspension of compound 3 (0.1 g) in water (10 ml) was treated 10 % sodium hydroxide solution (10 mL), and the mixture was heated at 80°, cooled, made neutral with acetic acid, and kept overnight at room temperature. The product was filtered off, washed with water, and recrystallized from ethanol-water, to give pale yellow needles (Table 5).

RESULTS AND DISCUSSION

Condensation of dehydro-*L*-ascorbic acid (*L-threo*-2-3-hexodiulosono-1,4-lactone) (1) with one molar proportion of *o*-bromophenylhydrazine or *o*-chlorophenylhydrazine at room temperature, afforded *L-threo*-2,3-hexodiulosono-1,4-lactone 2-arylhydrazone (2). The infrared spectra of 2 showed the lactone band at 1730 cm^{-1} in addition to a carbonyl absorption at 1680 cm^{-1}. On traetment of these with hydroxylamine, *L-threo*-2,3-hexodiulosono-1,4-lactone 2-arylhydrazone 3-oximes (3) were obtained. Boiling of compound 3 with acetic anhydride or treatment with acetic

Table 6. 1H-N.M.R. data for the compounds prepared.

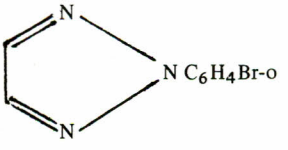
Compound	H-3	H-2	H-1	Aryl	Others
4a	4.46m	5.46q	5.89d	7.52-8.16m	2.06, 2.10 (2s, 2X3H, 2OCOCH$_3$)
4b	4.36m	5.38q	5.84d	7.46-8.1 m	2.04, 2.11 (2s, 2X3H, 2OCOCH$_3$)
6a	4.42m	5.39q	5.82d	7.46-8.2 m	2.02, 2.06, 2.11 (3s, 3X3H, 3OCOCH$_3$)
6b	4.46m	5.48q	5.90d	7.38-8.08m	2.02, 2.05, 2.13 (3s, 3X3H, 3OCOCH$_3$)
7a	4.38m	5.42q	5.88d	7.58-8.12m	2.02, 2.04, 2.13 (3s, 3X3H, 3OCOCH$_3$), 2.62 (s, 3H, NCOCH$_3$)
7b	4.44m	5.38q	5.82d	7.48-8.22m	2.01, 2.04, 2.12 (3s,3X3H, 3OCOCH$_3$),2.64 (s, 3H, NCOCH$_3$)
10a			5.58s	7.51-8.10m	2.12 (s, 3H, OCOCH$_3$)
10b			5.62s	7.36-8.12m	2.14 (s, 3H, OCOCH$_3$)
11a			5.62s	7.36-8.12m	2.14 (s, 3H, OCHOCH$_3$), 2.60 (s, 3H, NCOCH$_3$)
11B			5.53s	7.45-8.14m	2.14 (s, 3H, OCOCH$_3$), 2.60 (s, 3H, NCOCH$_3$)
15a	3.68m	5.82m	6.36d	7.16-7.82m	2.0 (s, 3H,)OCOCH$_3$)
15b	3.74m	5.88m	6.42d	7.18-8.0m	2.04 (s, 3H, OCOCH$_3$)

3-(Tri-O-acetyl-L-threo-glycerol-l-yl)-4,5-isoxazolinedione 4-(arylhydrazone) (17).--- A solution of compound 16 (0.1 g) in dry pyridine (5 mL) was treated with acetic anhydride (5 mL), and kept overnight at room temperature. The mixture was poured onto crushed ice, and the product was filtered off, washed with water, and dried. It was recrystallized from ethanol in pale yellow needles (Table 5).

L-threo-2,3-Hexodiulosono-1,4-lactone-2,3-bis(arylhydrazone) (18).--- A solution of dehydro-*L*-ascorbic acid (10 g) in water (100 mL) was treated with the desired arylhydrazine (10 g) and few drops of acetic acid, and heated on a steam bath for 3 h. The red solid was filtered off, washed with water, and dried. It was recrystallized from chloroform ethanol, giving red needles (Table 6).

3,6-Anhydro-derivatives (19).--- A suspension of compound 18 (0.1 g) in ethanol (20 mL) was treated with a solution of cupric chloride (1 g) in ethanol (20 mL) and heated under reflux for 1 h, cooled, water (10 mL) was added, and the solid was filtered off, washed with water, and dried. It was recystallized from ethanol, to give yellow needles (Table 6).

Table 7. Selected ions in the mass spectrum of compound 6a

ION	m/z
M + 1	483 (25); 485 (25)
M	482 (100); 484 (100)
M– CH_2CO + H	441 (16); 443 (16)
M– CH_2CO	440 (81); 442 (81)
M– HOAc + H	423 (32), 425 (32)
M– HOAc	422 (64); 424 (64)
M– 2 CH_2CO	402 (32); 404 (32)
M– 2 CH_2CO –H_2O	384 (50); 386 (50)
M– 3 CH_2CO	362 (38); 364 (38)
M– 3 CH_2CO	344 (41); 346 (41)
	222 (22); 224 (22)
NNC_6H_4Br-o	183-(23); 185 (23)
C_6H_4Br-o	155 (61); 157 (61)

anhydride and pyridine, resulted in the acetylation of the hydroxyl groups on C-5 and C-6 and elimination of a molecule of water from the hydrazone residue and the hydroxylamino group, to form 2-aryl-4-(L-threo-2,3-diacetoxy-1-hydroxypropyl)-1,2,3-triazole 5-carboxylic acid lactone (4). compounds 4 are the first triazole derivatives containing *o*-bromo- and *o*-chlorophenyl in the sugar series. This reaction is similar to that conducted [7,8] on the phenyl derivative. The infrared spectra of compound 4 showed the lactone band at 1800 cm^{-1} in addition to an ester band at 1740 cm^{-1}. The n.m.r. spectra of compounds 4 showed two acetyl group signals between δ 2.0 and 2.14 (Table 6).

Treatment of triazole 4 with liquid ammonia, deacetylation occurred with opening the lactone ring, to afford 2-aryl-4-(*L-threo*-1,2,3-trihydroxypropyl)-1,2,3-triazole 5-carboxamides (5). Mild acetylation of compounds 5 with acetic anhydride pyridine afforded triacetates designated 2-aryl-4-(1,2,3-tri-O-acetyl-*L-threo*-glycerol-1-yl)-1,2,3-triazole 5-carboxamides (6). The infrared spectra of 6 showed an amide band at 1680 cm^{-1}, in addition to an ester band at 1740 cm^{-1}. The mass spectrum of compound 6a showed a molecular ion peak at m/z 482, 484 followed by a series of ions arising from elimination processes involving the sugar moiety attached to the nitrogen heterocyclic, in addition to some fragmentation involving the heterocyclic ring (Table 7).

On the other hand, vigorous acetylation of compounds 5 with boiling acetic anhydride, afforded the tetra-acetates (7). The n.m.r. spectra of compounds 7 showed three O-acetyl group signals between δ 2.0 and 2.18, in addition to an N-acetyl group signal at δ 2.60 and 2.62.

Periodate oxidation of one mol of compound 5 resulted in the consumption of two mols of the oxidant with the formation of 2-aryl-4-formyl-1,2,3-triazole 5-carboxamides (8). Reduction of compounds 8 with sodium borohydride, afforded the 2-aryl-4-hydroxymethyl-1,2,3-triazole 5-carboxamides (9). Similarly, acetylation of compounds 9 with acetic anhydride in pyridine, afforded the 4-acetoxymethyl-2-aryl-1,2,3-triazole 5-carboxamides (10), whereas, vigorous acetylation with boiling acetic anhydride gave the diacetates (11).

Treatment of compound 3 with bromine-water, caused its cyclization, to give the triazole (12), its infrared spectra showed the hydroxyl absorption at 3450 cm^{-1} and the lactone carbonyl at 1800 cm^{-1}.

Treatment of compound 3 with hydrogen bromide-acetic acid, gave 5-*O*-acetyl-6-bromo-6-deoxy-*L-threo*-2,3-hexodiulosono-1,4-lactone 2-arylhydrazone 3-oxime (14) The infrared spectra of compounds 14 showed a band at 1740 cm^{-1} due to the lactone and ester groups. On boiling with acetic anhydride, compounds 14 are cyclized to 4-(2-*O*-acetyl-3-bromo-3-deoxy-*L-threo*-glycerol-1-yl)-2-aryl-1,2,3-triazole 5-carboxylic acid lactone (15).

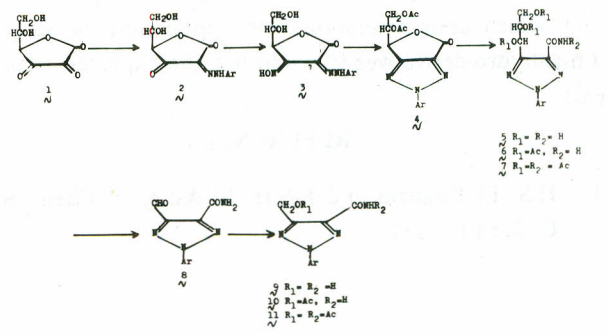


Fig. 1.

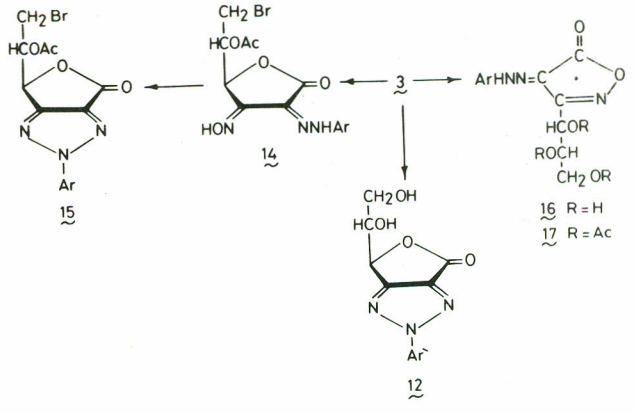


Fig. 2.

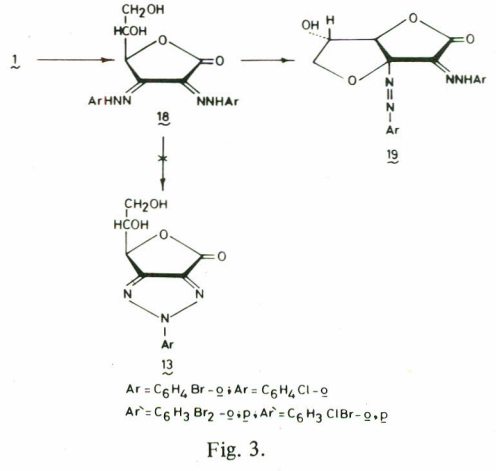


Fig. 3.

On treatment of compounds (3) with sodium hydroxide followed by neutralization, opening of the lactone ring occurred, followed by elimination of a molecule of water, affording 3-(*L-threo*-glycerol-1-yl)-4,5-isoxazolinedione 4-arylhydrazone ((16)). Acetylation of 16 with acetic anhydride pyridine, gave 3-(*L-threo*-1,2,3-tri-*O*-acetoxypropyl)-4,5-isoxazolinedione 4-arylhydrazone ((17)).

Treatment of dehydro-L-ascorbic acid (1) with two equivalents of arylhydrazine, afforded the bishydrazone ((18)), which upon oxidation with cupric chloride, gave the 3,6-anhydro-derivatives ((19)) and not the expected triazoles ((13)).

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