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

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ABSTRACT

L-*threo*-2,3-Hexodiulosono-1,4-lactone 2-(arylhydrazones) (**2**) were prepared by condensation of dehydro-L-ascorbic acid with various arylhydrazines. Reaction of **2** with hydroxylamine gave the 2-(arylhydrazone) 3-oximes (**3**). On boiling with acetic anhydride, **3** gave 2-aryl-4-(2,3-di-*O*-acetyl-L-*threo*-glycerol-1-yl)-1,2,3-triazole-5-carboxylic acid 5,4[1]-lactones (**4**). On treatment of **4** with liquid ammonia, 2-aryl-4-(L-*threo*-glycerol-1-yl)-1,2,3-triazole-5-carboxamides (**5**) were obtained. Acetylation of **5** with acetic anhydride–pyridine gave the triacetates, and vigorous acetylation with boiling acetic anhydride gave the tetraacetyl derivatives. Periodate oxidation of **5** gave the 2-aryl-4-formyl-1,2,3-triazole-5-carboxamides (**8**), and, on reduction, **8** gave the 2-aryl-4-(hydroxymethyl)-1,2,3-triazole-5-carboxamides, characterized as the monoacetates and diacetates. Controlled reaction of **2** with sodium hydroxide, followed by neutralization, gave 3-(L-*threo*-glycerol-1-yl)-4,5-isoxazolinedione 4-(arylhydrazones), characterized by their triacetates. Reaction of **2** with HBr–HOAc gave 5-*O*-acetyl-6-bromo-6-deoxy-L-*threo*-2,3-hexodiulosono-1,4-lactone 2-(arylhydrazones); these were converted into 4-(2-*O*-acetyl-3-bromo-3-deoxy-L-*threo*-glycerol-1-yl)-2-aryl-1,2,3-triazole-5-carboxylic acid 5,4[1]-lactones on treatment with acetic anhydride–pyridine.

INTRODUCTION

It is known that sugar osazones readily undergo cyclization to triazoles[2,3] on treatment with such heavy-metal salts as copper sulfate. Bromine[3] in water brings about the same conversion, with subsequent bromination at the para position of the phenyl group whenever it is free. On the other hand, oxidation of dehydro-L-ascorbic acid bishydrazones yields bicyclic azo compounds[4]. The triazole derivatives

*Triazole Derivatives from Dehydroascorbic Acids, Part IV. For Part III, see ref. 1.

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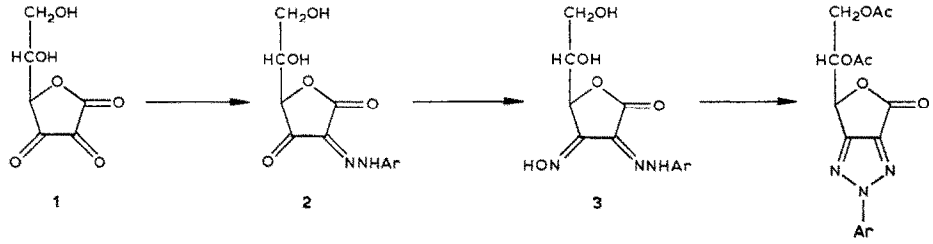
of dehydro-L-ascorbic acid and its 5-epimer have recently been prepared[1,5,6] through dehydrative cyclization of its 3-oxime 2-phenylhydrazone. Similarly, the *p*-bromophenyl analogs were prepared by the action of bromine in water thereon[1]. The insecticidal properties of 2-(*p*-chlorophenyl)- and 2-(*m*-chlorophenyl)-1,2,3-triazoles have been discussed[7], and, as a continuation of our work[8-11] on the synthesis of nitrogen heterocycles from dehydro-L-ascorbic acid and analogs[11], we now describe the synthesis and some reactions of the 2-aryltriazoles prepared from dehydro-L-ascorbic acid 2-arylhydrazone 3-oximes; derivatives possessing the *p*-chlorophenyl, *p*-tolyl, and *p*-nitrophenyl substituents have been prepared.

DISCUSSION AND RESULTS

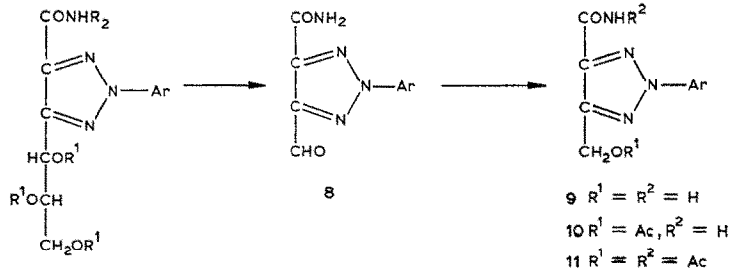
Unimolecular condensation of dehydro-L-ascorbic acid (L-*threo*-2,3-hexodiulosono-1,4-lactone) (**1**) with the selected substituted-phenylhydrazine at room temperature afforded L-*threo*-2,3-hexodiulosono-1,4-lactone 2-arylhydrazones (**2**). Derivatives possessing *p*-chlorophenyl[12], *p*-tolyl[12], and *p*-nitrophenyl substituents have been prepared; on treatment of these with hydroxylamine, L-*threo*-2,3-hexodiulosono-1,4-lactone 2-arylhydrazone 3-oximes (**3**) were obtained. Dehydrative cyclization and concomitant acetylation of **3** with boiling acetic anhydride gave the 2-aryl-4-(2,3-di-*O*-acetyl-L-*threo*-glycerol-1-yl)-1,2,3-triazole-5-carboxylic acid 5,4[1]-lactones (**4**). This reaction is similar to that conducted[5] on the phenyl derivative. The infrared spectra of **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 distinct, acetyl-group signals between δ 2.0 and 2.16 (see Table IX).

On treatment of **4** with liquid ammonia, deacetylation occurred concurrently with opening of the lactone ring, to afford the 2-aryl-4-(L-*threo*-glycerol-1-yl)-1,2,3-triazole-5-carboxamides (**5**). The infrared spectra of compounds **5** showed the amide band at 1690–1680 cm^{-1}, in addition to the hydroxyl band at 3500–3400 cm^{-1} (see Table III); the lactone band at 1800 cm^{-1} of the starting compounds had disappeared.

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 1690–1685 cm^{-1}, in addition to an ester band at 1740 cm^{-1}. The n.m.r. spectra of compounds **6** showed three separated acetyl-group signals between δ 2.0 and 2.16, in addition to those expected for the other protons (see Table IX). On the other hand, vigorous acetylation of compounds **5** with boiling acetic anhydride afforded tetraacetates (**7**), as indicated on the basis of elemental analysis, and n.m.r.- and mass-spectral data. The n.m.r. spectra of compounds **7** showed three *O*-acetyl-group signals between δ 2.00 and 2.18, in addition to an *N*-acetyl-group signal at δ 2.60–2.64. The mass spectrum of **7b** showed a molecular-ion peak (also the base peak), at *m/z* 460, corresponding to structure **7b**. This was followed by a series of ions arising from the elimination processes involving the sugar moiety attached to the nitrogen hetero-



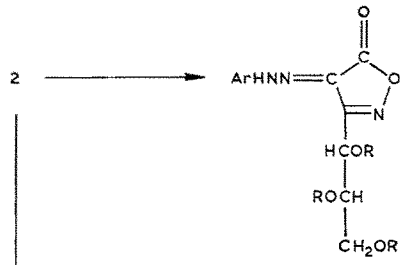
1 2 3 4



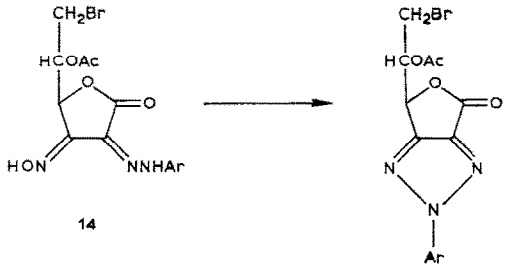
5 $R^1 = R^2 = H$
6 $R^1 = Ac, R^2 = H$
7 $R^1 = R^2 = Ac$

8

9 $R^1 = R^2 = H$
10 $R^1 = Ac, R^2 = H$
11 $R^1 = R^2 = Ac$



12 R = H
13 R = Ac



14 15

(a) Ar = C_6H_4Cl-*p*, (b) Ar = C_6H_4Me-*p*, (c) Ar = $C_6H_4NO_2$-*p*, (d) Ar = Ph

cycle. In addition, there was some fragmentation involving the heterocyclic ring (see Table X).

Periodate oxidation of one mol of compound **5** resulted in the consumption of two mol of the oxidant, with the formation of 2-aryl-4-formyl-1,2,3-triazole-5-carboxamides (**8**). The infrared spectra of **8** showed a broad band at 1700–1680 cm^{-1} due to the aldehyde and the amide group (see Table V). 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 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**). The mass spectrum of compound **11a** (see Table XI) showed a molecular-ion peak at *m/z* 336, 338, in addition to a series of ions arising from elimination processes in the side chain and in the heterocyclic ring.

On controlled treatment of compounds **3** with sodium hydroxide, followed by acidification, 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-arylhydrazones (**12**). The infrared spectra of compounds **12** showed carbonyl absorption at 1725–1720 cm^{-1}, and, in addition, hydroxyl absorption at 3460–3420 cm^{-1} (see Table VII). The mass spectrum of **12a** showed a molecular ion-peak at *m/z* 313, 315 (which is the base peak), followed by a series of ions arising from elimination processes involving the sugar moiety attached to the nitrogen heterocyclic. Ions arising from elimination of the chlorine atom, and cleavage in the sugar portion were also noted, in addition to some fragmentation involving the heterocyclic ring (see Table XII).

Treatment of compound **3** with hydrogen bromide in acetic acid gave 5-*O*-acetyl-6-bromo-6-deoxy-L-*threo*-2,3-hexodiulosono-1,4-lactone 2-arylhydrazone 3-oximes (**14**). The infrared spectra of compounds **14** showed a band at 1740 cm^{-1} due to the lactone and ester groups, in addition to the hydroxyl absorption at 3350–3320 cm^{-1}. On boiling with acetic anhydride, compounds **14** were dehydratively cyclized to 4-(2-*O*-acetyl-3-bromo-3-deoxy-L-*threo*-glycerol-1-yl)-2-aryl-1,2,3-triazole-5-carboxylic acid 5,4[1]-lactone (**15**). The infrared spectrum of **15** showed the lactone band at 1800 cm^{-1} and the ester band at 1740 cm^{-1}, and the n.m.r. spectrum showed one acetyl-group signal, at δ 2.00–2.02 (see Table IX).

EXPERIMENTAL

General methods. — Melting points were determined with a Tottoli (Büchi) apparatus and are uncorrected. I.r. spectra were recorded with a 580 B Perkin–Elmer spectrometer, and n.m.r. spectra (for solutions in chloroform-*d*), with tetramethylsilane as the standard, with R 12 B Perkin–Elmer and 250 Cameca spectrometers. Chemical shifts are given on the δ scale. Mass spectra were recorded with an LKB 2091 spectrometer; intensities are given in parentheses, as percentages of the base

TABLE I

MICROANALYTICAL AND I.R. DATA FOR 2-ARYLHYDRAZONES (2) AND OXIMES (3)

Compound	*Ar*	*M.p. (degrees)*	*Molecular formula*	*Analysis*				*ν (cm⁻¹)*			
				C	*H*	*Hal.*	*N*	*OH*	*lactone*	*C=O*	*C=N*
2a	C_6H_4Cl-*p*	200–201[a]									
2b	C_6H_4Me-*p*	172–173[b]									
2c	$C_6H_4NO_2$-*p*	189–190	$C_{12}H_{11}N_3O_7$	Calc. 46.61	3.58		13.58	3400	1720	1680	1610
				Found 46.72	3.46		13.49				
3a	C_6H_4Cl-*p*	235–236	$C_{12}H_{12}ClN_3O_5$	Calc. 45.94	3.85	11.30	13.38	3330	1750		1600
				Found 45.95	3.86	11.42	13.28				
3b	C_6H_4Me-*p*	241–242	$C_{13}H_{15}N_3O_5$	Calc. 53.24	5.15		14.32	3400	1750		1600
				Found 53 21	5.17		14.27				
3c	$C_6H_4NO_2$-*p*	231–232	$C_{12}H_{12}N_4O_7$	Calc. 44.45	3.73		17.27	3500	1750		1600
				Found 44.55	3.81		17.03				

[a]Lit.[12] m.p. 203–204°. [b]Lit.[12] m.p. 172–173°.

TABLE II

MICROANALYTICAL AND I.R. DATA FOR TRIAZOLES (**4**)

Compound	*Ar*	*M.p. (degrees)*	*Molecular formula*	*Analysis*				*ν (cm⁻¹)*		
				C	*H*	*Cl*	*N*	*lactone*	*ester*	*C=N*
4a	C_6H_4Cl-*p*	87–88	$C_{16}H_{14}ClN_3O_6$	Calc. 50.60	3.71	9.33	11.07	1800	1740	1600
				Found 50.61	3.65	9.69	11.26			
4b	C_6H_4Me-*p*	67–68	$C_{17}H_{17}N_3O_6$	Calc. 56.82	4.76		11.68	1800	1740	1610
				Found 56.74	4.52		11.46			
4c	$C_6H_4NO_2$-*p*	135–136	$C_{16}H_{14}N_4O_8$	Calc. 49.24	3.61		14.34	1800	1740	1600
				Found 49.29	3.57		14.22			

TABLE III

MICROANALYTICAL AND I.R. DATA FOR TRIAZOLECARBOXAMIDES (**5**)

Compound	*Ar*	*M.p. (degrees)*	*Molecular formula*	*Analysis*				*ν (cm⁻¹)*			
				C	*H*	*Cl*	*N*	*OH*	*NH*	*CON*	*C=N*
5a	C_6H_4Cl-*p*	190–192	$C_{12}H_{13}ClN_4O_4$	Calc. 46.09	4.19	11.34	17.91	3350	3200	1685	1610
				Found 46.23	4.09	11.17	17.59				
5b	C_6H_4Me-*p*	185–186	$C_{13}H_{16}N_4O_4$	Calc. 53.42	5.51		19.16	3380	3200	1690	1610
				Found 53.32	5.45		19.15				
5c	$C_6H_4NO_2$-*p*	194–195	$C_{12}H_{13}N_5O_6$	Calc. 44.58	4.02		21.67	3440	3180	1680	1600
				Found 44.52	3.89		21.45				

TABLE IV

MICROANALYTICAL AND I.R. DATA FOR TRIAZOLE ACETATES (6 AND 7)

Compound	*Ar*	*M.p. (degrees)*	*Molecular formula*	*Analysis*				*ν (cm⁻¹)*		
				C	*H*	*Cl*	*N*	*NH*	*ester*	*CON*
6a	C_6H_4Cl-*p*	177–178	$C_{18}H_{19}ClN_4O_7$	Calc. 49.26	4.36	8.07	12.76	3200	1740	1690
				Found 49.43	4.43	7.90	12.96			
6b	C_6H_4Me-*p*	122–123	$C_{19}H_{22}N_4O_7$	Calc. 54.54	5.30		13.38	3180	1740	1690
				Found 54.29	5.03		13.02			
6c	$C_6H_4NO_2$-*p*	211–212	$C_{18}H_{19}N_5O_9$	Calc. 48.11	4.26		15.57	3180	1740	1685
				Found 48.05	4.16		15.58			
7a	C_6H_4Cl-*p*	158–159	$C_{20}H_{21}ClN_4O_8$	Calc. 49.95	4.40		11.64	3180	1740	1690
				Found 49.72	4.56		11.78			
7b	C_6H_4Me-*p*	168–169	$C_{21}H_{24}N_4O_8$	Calc. 54.78	5.25		12.16	3180	1740	1690
				Found 54.62	5.08		12.46			
7c	$C_6H_4NO_2$-*p*	202–203	$C_{20}H_{21}N_5O_{10}$	Calc. 48.88	4.30		14.24	3200	1740	1690
				Found 48.62	4.54		14.62			

TABLE V

MICROANALYTICAL AND I.R. DATA FOR TRIAZOLE ALDEHYDES (**8**) AND TRIAZOLE ALCOHOLS (**9**)

Compound	*Ar*	*M.p. (degrees)*	*Molecular formula*	*Analysis*				*ν (cm⁻¹)*		
				C	*H*	*Cl*	*N*	*OH*	*NH*	*(CON + COH)*
8a	C_6H_4Cl-*p*	205–206	$C_{10}H_7ClN_4O_2$	Calc. 47.92	2.81	14.14	22.34		3200	1700
				Found 47.52	2.99	14.11	21.94			
8b	C_6H_4Me-*p*	201–202	$C_{11}H_{10}N_4O_2$	Calc. 57.39	4.37		24.32		3200	1680
				Found 57.72	4.50		24.52			
8c	$C_6H_4NO_2$-*p*	177–178	$C_{10}H_7N_5O_4$	Calc. 45.98	2.70		26.82		3200	1690
				Found 45.72	2.62		26.54			
9a	C_6H_4Cl-*p*	218–219	$C_{10}H_9ClN_4O_2$	Calc. 47.54	3.59	14.03	22.16	3320	3180	1685
				Found 47.47	3.83	14.05	22.07			
9b	C_6H_4Me-*p*	150–151	$C_{11}H_{12}N_4O_2$	Calc. 56.89	5.20		24.11	3400	3180	1680
				Found 56.72	5.06		24.36			
9c	$C_6H_4NO_2$-*p*	217–218	$C_{10}H_9N_5O_4$	Calc. 45.63	3.44		26.59	3300	3200	1680
				Found 45.74	3.32		26.72			

TABLE VI

MICROANALYTICAL AND I.R. DATA FOR TRIAZOLE ACETATES (**10** AND **11**)

Compound	*Ar*	*M.p. (degrees)*	*Molecular formula*	*Analysis*				*ν (cm⁻¹)*		
				C	*H*	*Cl*	*N*	*NH*	*ester*	*CON*
10a	C_6H_4Cl-*p*	160–161	$C_{12}H_{11}ClN_4O_3$	Calc. 48.91	3.76	12.03	19.00	3180	1740	1690
				Found 49.26	3.75	12.32	18.71			
10b	C_6H_4Me-*p*	132–133	$C_{13}H_{14}N_4O_3$	Calc. 56.93	5.14		20.40	3200	1740	1690
				Found 56.72	5.36		20.68			
10c	$C_6H_4NO_2$-*p*	196–197	$C_{12}H_{11}N_5O_5$	Calc. 47.22	3.63		22.93	3200	1740	1690
				Found 47.15	3.49		22.43			
11a	C_6H_4Cl-*p*	177–178	$C_{14}H_{13}ClN_4O_4$	Calc. 49.94	3.89	10.52	16.63	3160	1740	1680
				Found 50.21	3.79	10.22	16.46			
11b	C_6H_4Me-*p*	150–151	$C_{15}H_{16}N_4O_4$	Calc. 56.96	5.09		17.70	3180	1740	1685
				Found 56.71	5.23		17.42			
11c	$C_6H_4NO_2$-*p*	174–175	$C_{14}H_{13}N_5O_6$	Calc. 48.42	3.77		20.16	3200	1740	1690
				Found 48.12	3.61		20.38			

peak. Microanalyses were performed in the Service Central d'Analyse du CNRS, France.

L-threo-*2,3-Hexodiulosono-1,4-lactone 2-(arylhydrazones)* (**2**). — A solution of dehydro-L-ascorbic acid (**1**; 0.05 mol) in water (100 mL) was treated with the chosen arylhydrazine (0.05 mol). The mixture was kept for 24 h at room temperature; the monohydrazone that had separated out was filtered off, successively washed with water, ethanol, and ether, and dried. Recrystallization from ethanol gave compounds **2** as yellow needles. Melting points, formulas, analyses, and i.r. data are listed in Table I.

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 g) and sodium acetate (1 g), and the mixture was boiled under reflux for 3 h. It was then concentrated, water (20 mL) was added, and the solid that separated out was filtered off, washed successively with water, ethanol, and ether, and dried. Each compound was recrystallized from ethanol, giving yellow needles. Melting points, formulas, analyses, and i.r. data are listed in Table I.

*2-Aryl-4-(2,3-di-*O*-acetyl-*L-threo-*glycerol-1-yl)-1,2,3-triazole-5-carboxylic acid 5,4*^{1}*-lactone* (**4**). — (*a*) A suspension of each compound **3** (1 g) in dry pyridine (20 mL) was treated with acetic anhydride (10 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, to give colorless needles (see Table II). N.m.r. data are listed in Table IX.

(*b*) A suspension of compound **3** (0.1 g) in acetic anhydride (10 mL) was boiled under reflux for 30 min. The mixture was poured onto crushed ice, and the product that separated was filtered off, successively washed with water and ethanol, and dried. The product was recrystallized from ethanol, to give colorless needles, identical with those obtained by method *a*.

2-Aryl-4-(L-threo-*glycerol-1-yl)-1,2,3-triazole-5-carboxamides* (**5**). — A solution of compound **4** (1 g) in methanol (20 mL) was treated with concentrated ammonia (20 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–chloroform, to give colorless needles (see Table III).

*2-Aryl-4-(1,2,3-tri-*O*-acetyl-*L-threo-*glycerol-1-yl)-1,2,3-triazole-5-carboxamide* (**6**). — A solution of each compound **5** (0.1 g) in dry pyridine (10 mL) was treated with acetic anhydride (5 mL), and kept overnight at room temperature. The mixture was poured onto crushed ice, and the solid that separated was filtered off, successively washed with water and ethanol, and recrystallized from ethanol, to give colorless needles. Melting points, formulas, analyses, and i.r. data are listed in Table IV, and n.m.r. data in Table IX.

Triazole tetraacetates (**7**). — A suspension of each compound **5** (0.1 g) in acetic anhydride (10 mL) was boiled under reflux for 1 h. The mixture was then cooled,

and poured onto crushed ice, and the product that separated was filtered off, washed successively with water and ethanol, and dried. The products were recrystallized from ethanol, giving colorless needles. Melting points, formulas, analyses, and i.r. spectra are listed in Table IV, and n.m.r. data in Table IX. Mass-spectral data for compound **7b** are given in Table X.

2-Aryl-4-formyl-1,2,3-triazole-5-carboxamides (**8**). — A suspension of each compound **5** (0.3 g) in water (30 mL) was treated with a solution of sodium metaperiodate (1 g) in water (20 mL), and the mixture was shaken for 24 h. The solid that separated was filtered off, washed with water, and dried. Each product was recrystallized from chloroform–ethanol, giving colorless prisms. Melting points, formulas, analyses, and i.r. data are listed in Table V.

2-Aryl-4-(hydroxymethyl)-1,2,3-triazole-5-carboxamide (**9**). — A solution of each compound **8** (0.1 g) in methanol (20 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 acetic acid, and the solid that separated was filtered off, washed with water, and dried. It was recrystallized from methanol, to give colorless needles (see Table V).

4-(Acetoxymethyl)-2-aryl-1,2,3-triazole-5-carboxamides (**10**). — A solution of each compound **9** (0.1 g) in dry pyridine (10 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, successively washed with water, ethanol, and ether, and dried. Each product was recrystallized from ethanol, to give colorless needles. Melting points, formulas, analyses, and i.r. data are listed in Table VI.

Triazole diacetates (**11**). — A suspension of each compound **9** (0.1 g) in acetic anhydride (10 mL) was boiled under reflux for 2 h. The mixture was poured onto crushed ice, and the product was filtered off, washed with water, and dried. Recrystallization from ethanol gave compounds **11** as colorless needles (see Table VI). N.m.r. data are listed in Table IX, and mass-spectral data for compound **11a**, in Table XI.

TABLE VII

MICROANALYTICAL AND I.R. DATA FOR ISOXAZOLINEDIONES (**12**) AND ACETATES (**13**)

Compound	*Ar*	*M.p. (degrees)*	*Molecular formula*	*Analysis*	*C*	*H*	*N*	*ν (cm⁻¹) OH*	*CO*
12a	C_6H_4Cl-*p*	170–171	$C_{12}H_{12}ClN_3O_5$	Calc.	45.94	3.85	13.38	3420	1725
				Found	45.72	3.76	13.20		
12b	C_6H_4Me-*p*	192–193	$C_{13}H_{15}N_3O_5$	Calc.	53.24	5.15	14.32	3460	1720
				Found	53.36	5.24	14.46		
12d	C_6H_5	150–151	$C_{12}H_{13}N_3O_5$	Calc.	51.61	4.69	15.04	3400	1725
				Found	51.20	4.60	14.84		
13d	C_6H_5	syrup	$C_{18}H_{19}N_3O_8$	Calc.	53.33	4.72	10.36		1730
				Found	53.71	4.52	10.58		

TABLE VIII

MICROANALYTICAL AND I.R. DATA FOR COMPOUNDS **14** AND **15**

Compound	*Ar*	*M.p. (degrees)*	*Molecular formula*	*Analysis*			*ν (cm⁻¹)*		
				C	*H*	*N*	*lactone*	*(lactone + ester)*	*ester*
14a	C_6H_4Cl-*p*	206–207	$C_{14}H_{13}BrClN_3O_5$	Calc. 40.16	3.13	10.03		1740	
				Found 40.45	3.32	10.42			
14b	C_6H_4Me-*p*	216–218	$C_{15}H_{16}BrN_3O_5$	Calc. 45.24	4.05	10.54		1740	
				Found 45.46	4.32	10.74			
14c	$C_6H_4NO_2$-*p*	218–220	$C_{14}H_{13}BrN_4O_7$	Calc. 39.18	3.05	13.05		1740	
				Found 39.42	3.31	13.48			
15b	C_6H_4Me-*p*	117–118	$C_{15}H_{14}BrN_3O_4$	Calc. 47.38	3.71	11.04	1800		1740
				Found 47.65	3.82	11.31			
15c	$C_6H_4NO_2$-*p*	139–140	$C_{14}H_{11}BrN_4O_6$	Calc. 40.89	2.69	13.62	1800		1740
				Found 40.72	2.60	13.42			

TABLE IX

^{1}H-N.M.R. DATA FOR COMPOUNDS PREPARED

Compound	*H-3*	*H-3′*	*H-2*	*H-1*	*Aryl*	*Others*
4a	4.36 q	4.56 q	5.50 q	5.86 d	7.50–8.20 m	2.04, 2.1 (2 s, 2 × 3 H, 2 OAc)
4b	4.35 q	4.52 q	5.56 q	5.84 d	7.22–8.02 m	2.03, 2.09 (2 s, 2 × 3 H, 2 OAc); 2.41 (s, 3 H, CH_3)
4c	4.41 q	4.52 q	5.55 q	6.39 d	8.25–8.47 m	2.04, 2.15 (2 s, 2 × 3 H, 2 OAc)
6a	4.20 q	4.36 q	5.80 q	6.72 d	7.50–8.00 m	2.03, 2.08, and 2.16 (3 s, 3 × 3 H, 3 OAc)
6b	4.16 q	4.36 q	5.80 q	6.72 d	7.24–7.95 m	2.00, 2.04, and 2.13 (3 s, 3 × 3 H, 3 OAc; 2.58 (s, 3 H, CH_3)
6c	4.23 q	4.37 q	5.82 q	6.70 d	8.28–8.43 m	2.02, 2.07, and 2.18 (3 s, 3 × 3 H, 3 OAc)
7a	4.18 q	4.35 q	5.82 q	6.70 d	7.22–7.90 m	2.00, 2.04, and 2.15 (3 s, 3 × 3 H, 3 OAc); 2.60 s, 3 H, NAc)
7b	4.20 q	4.36 q	5.80 q	6.72 d	7.26–7.92 m	2.02, 2.06, and 2.14 (3 s, 3 × 3 H, 3 OAc); 2.42 (s, 3 H, CH_3); 2.62 (s, 3 H, NAc)
7c	4.20 q	4.36 q	5.80 q	6.70 d	8.26–8.41 m	2.02, 2.07, and 2.18 (3 s, 3 × 3 H, 3 OAc); 2.64 (s, 3 H, NAc)
10a				5.56 s	7.45–8.03 m	2.15 (s, 3 H, OAc)
10b				5.55 s	7.27–7.94 m	2.14 (s, 3 H, OAc); 2.41 (s, 3 H, CH_3)
10c				5.58 s	8.25–8.42 m	2.17 (s, 3 H, OAc)
11a				5.55 s	7.25–8.00 m	2.15 (s, 3 H, OAc); 2.62 (s, 3 H, NAc)
11b				5.53 s	7.26–7.95 m	2.15 (s, 3 H, OAc); 2.42 (s, 3 H, CH_3; 2.62 (s, 3 H, NAc)
11c				5.58 s	8.26–8.44 m	2.17 (s, 3 H, OAc); 2.62 (s, 3 H, NAc)
13d	4.20 q	4.44 q	5.92 q	6.22 d	7.20–7.60 m	2.08, 2.10, and 2.18 (3 s, 3 × 3 H, 3 OAc), and 12.69 (NH)
14a	3.66 m		5.82 m	6.46 d	7.24–7.92 m	2.02 (s, 3 H, OAc)
14b	3.60 m		5.75 m	6.95 d	7.16–7.32 m	2.00 (s, 3 H, OAc); 2.34 (s, 3 H, CH_3)
14c	3.62 m		5.81 m	6.77 d	7.25–7.72 m	2.00 (s, 3 H, OAc)
15b	3.72 m		4.44 m	6.01 d	7.31–8.03 m	2.01 (s, 3 H, OAc); 2.44 (s, 3 H, CH_3)
15c	3.70 m		4.46 m	6.68 d	7.21–7.79 m	2.02 (s, 3 H, OAc)

TABLE X

SELECTED IONS IN THE MASS SPECTRUM OF COMPOUND **7b**

Ion	m/z
M + 1	461 (25)
M	460 (100)
M − CH_2CO + H	419 (20)
M − CH_2CO	418 (70)
M − CH_3 − CH_2CO	403 (16)
M − HOAc + H	401 (45)
M − HOAc	400 (15)
M − HOAc − OH	383 (70)
M − HOAc − H_2O	382 (60)
M − 2 CH_2CO	376 (20)
M − 2 CH_2CO − H_2O	366 (90)
M − 3 CH_2CO − OH	317 (28)
M − 4 CH_2CO + 2 H	294 (36)
$N_3C_6H_4CH_3$	133 (70)
$N_2C_6H_4CH_3$	119 (62)
$NHC_6H_4CH_3$	105 (36)
$NC_6H_4CH_3$	104 (60)
$C_6H_4CH_3$	91 (70)

TABLE XI

SELECTED IONS IN THE MASS SPECTRUM OF COMPOUND **11a**

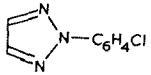
Ion	m/z
M + 1	337 (50); 339 (20)
M	336 (80); 338 (40)
M − CH_2CO	294 (100); 296 (30)
M − CH_2CO − O	278 (20); 280 (10)
M − Cl − CH_2CO	259 (40)
M − 2 CH_2CO	252 (80); 254 (40)
M − 2 CH_2CO − Cl	217 (8)
	178 (30); 180 (18)
$N_3C_6H_4Cl$	153 (12); 155 (8)
$N_2C_6H_4Cl$	139 (30); 141 (15)
HNC_6H_4Cl	126 (10); 128 (6)
NC_6H_4Cl	125 (20); 127 (12)
C_6H_4Cl	111 (70); 113 (30)

TABLE XII

SELECTED IONS IN THE MASS SPECTRUM OF COMPOUND **12a**

Ion	m/z
M	213 (100); 315 (30)
M − O	297 (60); 299 (20)
M − H_2O	295 (65); 297 (30)
M − CH_2OH	282 (60); 284 (25)
M − Cl	279 (15)
M − CH_2OH − O	266 (82); 268 (36)
M − CH_2OH − OH	265 (76); 267 (32)
M − CH_2OH − H_2O	264 (40); 266 (18)
M − CH_2OH − H_2O − H_2	262 (36); 264 (15)
M − CH_2OH − CHOH	252 (32); 254 (14)
M − Cl − CH_2OH	248 (22)
M − CH_2OH − CHOH − O	236 (40); 238 (18)
M − CH_2OH − CHOH − Cl	218 (64)
$N_3C_6H_4Cl$	153 (30); 155 (12)
$N_2C_6H_4Cl$	139 (28); 141 (17)
HNC_6H_4Cl	126 (10); 128 (6)
NC_6H_4Cl	125 (18); 127 (10)
C_6H_4Cl	111 (60); 113 (28)

3-(L-threo-*glycerol-1-yl)-4,5-isoxazolinedione 4-arylhydrazones* (**12**). — A suspension of each compound **2** (1 mmol) in water (10 mL) was treated with a 10% solution of sodium hydroxide (20 mL), and the mixture was heated for 15 min at 80°, cooled, acidified with acetic acid, and kept overnight at room temperature. The product was filtered off, washed with water, and recrystallized from ethanol, to give pale-yellow needles (see Table VII). Mass-spectral data for compound **12a** are given in Table XII.

*3-(Tri-*O-*acetyl-*L-threo-*glycerol-1-yl)-4,5-isoxazolinedione 4-phenylhydrazone* (**13d**). — A solution of 3-(L-*threo*-glycerol-1-yl)-4,5-isoxazolinedione 4-phenylhydrazone (**12d**; 0.1 g) in dry pyridine (10 mL) was treated with acetic anhydride (5 mL), and kept overnight at room temperature. The mixture was poured onto crushed ice, and a pure sample of the product was obtained by preparative t.l.c. on silica gel, using 1:3 (v/v) cyclohexane–methanol as the eluant (see Table VII). N.m.r. data are listed in Table IX.

*5-*O-*Acetyl-6-bromo-6-deoxy-*L-threo-*2,3-hexodiulosono-1,4-lactone 2-arylhydrazone 3-oximes* (**14**). — To each compound **3** (1 g) was added HBr–HOAc (20 mL), and the mixture was stirred for 24 h at room temperature. Water (100 mL) was added, and the solid that separated was filtered off, washed successively with water, ethanol, and ether, and dried. It was recrystallized from ethanol, to give colorless needles (see Table VIII). N.m.r. data are given in Table IX.

*2-Aryl-4-(2-*O-*acetyl-3-bromo-3-deoxy-*L-threo-*glycerol-1-yl)-1,2,3-triazole-5-carboxylic acid 5,4*^{1}*-lactone* (**15**). — A suspension of compound **14** (0.1 g) in

acetic anhydride (10 mL) was boiled under reflux for 30 min. The mixture was poured onto crushed ice, and the product that separated was filtered off, washed with water, and dried. Each product was recrystallized from ethanol, giving colorless needles. Melting points, formulas, analyses, and i.r. data are listed in Table VIII, and n.m.r. data in Table IX.

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