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

MOHAMED ALI EL SEKILY AND SOHILA MANCY
Department of Chemistry, Faculty of Science, Alexandria University, Alexandria (Egypt)
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ABSTRACT

D-*erythro*-2,3-Hexodiulosono-1,4-lactone 2-arylhydrazones (**2**) were prepared by condensation of dehydro-D-*arabino*-ascorbic acid with the desired arylhydrazine. 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-D-*erythro*-glycerol-1-yl)-1,2,3-triazole-5-carboxylic acid 5,1[1]-lactone (**5**), whereas the unacetylated triazole derivatives were obtained upon reaction of **3** with bromine in water. On treatment of **5** with hydrazine hydrate, 2-aryl-4-(D-*erythro*-glycerol-1-yl)-1,2,3-triazole-5-carboxylic acid 5-hydrazides (**6**) were obtained. Acetylation of **6** gave the hexaacetyl derivatives. Similarly, treatment of **5** with liquid ammonia gave the triazolecarboxamides (**12**). Vigorous acetylation of **12** with boiling acetic anhydride gave tetraacetates, whereas acetylation with acetic anhydride–pyridine gave triacetates. Periodate oxidation of **6** gave the 2-aryl-4-formyl-1,2,3-triazole-5-carboxylic acid 5-hydrazides (**8**), and, on reduction, **8** gave the 2-aryl-4-(hydroxymethyl)-1,2,3-triazole-5-carboxylic acid 5-hydrazides, characterized as acetates. Similarly, periodate oxidation of **12** gave the triazolealdehyde (**15**), and reduction of **15** gave the hydroxymethyl derivatives (**16**). Acetylation of **16** gave the mono- and di-acetates, and, on reaction with *o*-phenylenediamine, **15** afforded the triazoleimidazole. Controlled reaction of **3** with sodium hydroxide, followed by neutralization, gave 3-(D-*erythro*-glycerol-1-yl)-4,5-isoxazolinedione 4-arylhydrazones. Reaction of **3** with HBr–HOAc gave 5-*O*-acetyl-6-bromo-6-deoxy-D-*erythro*-2,3-hexodiulosono-1,4-lactone 2-arylhydrazone 3-oximes (**21**). Compounds **21** were converted into 4-(2-*O*-acetyl-3-bromo-3-deoxy-D-*erythro*-glycerol-1-yl)-2-aryl-1,2,3-triazole-5-carboxylic acid 5,1[1]-lactone on treatment with acetic anhydride.

DISCUSSION AND RESULTS

Because of our continued interest in the synthesis of nitrogen heterocycles

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

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from dehydro-L-ascorbic acid mono- and bis-hydrazones and analogs[1–6], we now describe the synthesis and reactions of the 2-aryltriazoles prepared from dehydro-D-*arabino*-ascorbic acid 2-arylhydrazone 3-oximes. Derivatives possessing the *p*-chlorophenyl, *p*-methoxyphenyl, *p*-tolyl, and phenyl substituents have been prepared, and the insecticidal properties of 2-(*p*-chlorophenyl)- and 2-(*m*-chlorophenyl)-1,2,3-triazoles have been evaluated[7].

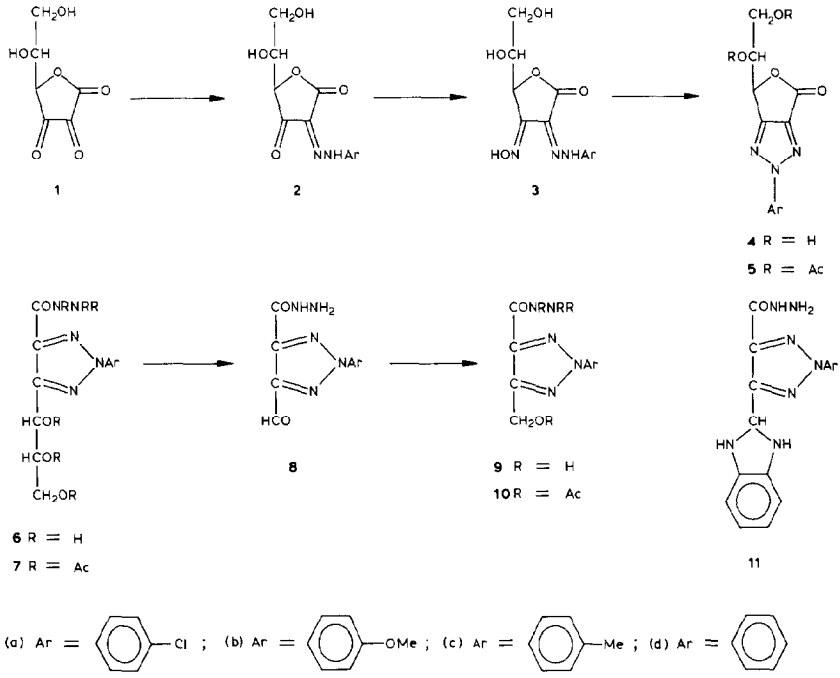
Unimolecular condensation of dehydro-D-*arabino*-ascorbic acid (D-*erythro*-2,3-hexodiulosono-1,4-lactone, **1**) with the desired hydrazine at room temperature afforded D-*erythro*-2,3-hexodiulosono-1,4-lactone 2-arylhydrazones (**2**). On treatment of **2** with hydroxylamine, D-*erythro*-2,3-hexodiulosono-1,4-lactone 2-arylhydrazone 3-oximes (**3**) were obtained, and these afforded 2-aryl-4-(2,3-di-*O*-acetyl-D-*erythro*-glycerol-1-yl)-1,2,3-triazole-5-carboxylic acid 5,1[1]-lactones (**5**) on treatment with boiling acetic anhydride or with acetic anhydride–pyridine; higher yields were obtained on using acetyl chloride–pyridine as the acylating, dehydrative-cyclizing agent.

The infrared spectra of **5** showed the lactone band at 1800 cm^{-1}, in addition to an ester band at 1750–1740 cm^{-1}. The n.m.r. spectra of **5** showed two singlets, corresponding to two acetyl groups, between δ 2.04 and 2.10 (see Table VII). The unacetylated triazole derivatives (**4**) were obtained on treatment of the hydrazone oxime **3** with bromine in water.

On treatment of compounds **5** with hydrazine hydrate in methanol, deacetylation occurred concurrently with opening of the lactone ring, to afford 2-aryl-4-(D-*erythro*-glycerol-1-yl)-1,2,3-triazole-5-carboxylic acid 5-hydrazides (**6**). The infrared spectra of **6** showed the amide band at 1680 cm^{-1}, in addition to the hydroxyl absorption at 3500–3450 cm^{-1} (see Table II). Acetylation of 4-(D-*erythro*-glycerol-1-yl)-2-*p*-tolyl-1,2,3-triazole-5-carboxylic acid 5-hydrazide (**6c**) with acetic anhydride in pyridine, or with boiling acetic anhydride, afforded a hexaacetyl derivative (**7c**), as indicated on the basis of elemental analysis, and by n.m.r.- and mass-spectral data. Its i.r. spectrum showed a band for the acetyl groups at 1750 cm^{-1}, in addition to one for the amide group at 1680 cm^{-1}, and its elemental analysis agreed with the molecular formula $C_{25}H_{29}N_5O_{10}$. The mass spectrum of **7c** showed a molecular-ion peak (also the base peak) at *m/z* 559, agreeing with the hexaacetyl derivative; and the ^{1}H-n.m.r. spectrum showed signals for three *O*-acetyl groups, at δ 2.05, 2.07, and 2.14, three *N*-acetyl groups, as signals at δ 2.37, 2.41, 2.45, and a singlet at δ 2.44 for the methyl group. The C-3 methylene group appeared as two quartets, of one-proton intensity each, at δ 4.14 and 4.38, the C-2 methine proton, as a quartet at δ 5.77, and the C-1 methine proton as a doublet at δ 6.57 ($J_{1,2}$ 6.5 Hz). The aromatic protons appeared as a multiplet at δ 7.26–7.84, and there were no NH signals. Similar treatment of compounds **6a**, **6b**, and **6d** gave the corresponding hexaacetates (**7a**, **7b**, and **7d**, respectively).

Periodate oxidation of one mol of compound **6** resulted in the consumption of two mol of the oxidant, with the formation of 2-aryl-4-formyl-1,2,3-triazole-5-carboxylic acid 5-hydrazides (**8**). The i.r. spectra showed an unresolved band at

1700–1690 cm^{-1}, due to the aldehyde and the amide group. Reduction of **8** with sodium borohydride afforded the 2-aryl-4-(hydroxymethyl)-1,2,3-triazole-5-carboxylic acid 5-hydrazides (**9**), characterized as the acetates (**10**).

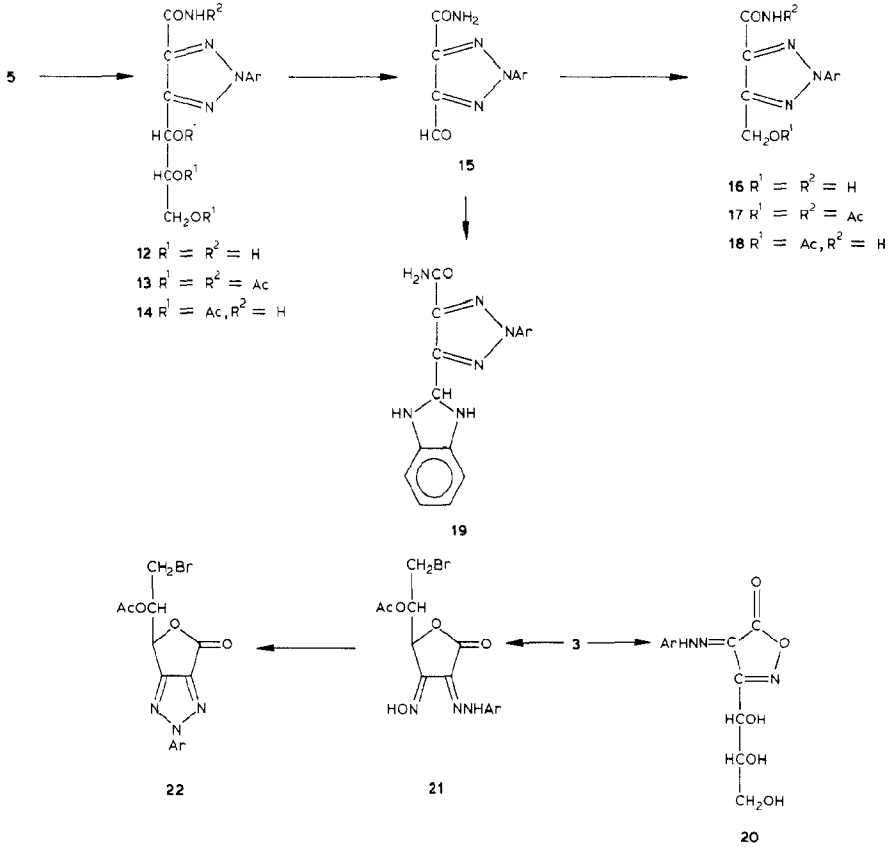


Similarly, treatment of the triazoles **5** with liquid ammonia afforded 2-aryl-4-(D-*erythro*-glycerol-1-yl)-1,2,3-triazole-5-carboxamides (**12**) (see Table III). Vigorous acetylation of **12** with boiling acetic anhydride afforded the tetraacetates (**13**) on the basis of elemental analysis, and n.m.r.- and mass-spectral data. The n.m.r. spectra of compounds **13** 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 (see Table VII). The mass spectrum of compound **13c** showed a molecular-ion peak (also the base peak) at *m/z* 460, corresponding to structure **13c**; this was followed by a series of ions arising from the elimination processes involving the sugar moiety attached to the nitrogen heterocycle (see Table IX). Mild acetylation of **12** with acetic anhydride–pyridine afforded the triacetates designated 2-aryl-4-(1,2,3-tri-*O*-acetyl-D-*erythro*-glycerol-1-yl)-1,2,3-triazole-5-carboxamides (**14**). Periodate oxidation of 4-(D-*erythro*-glycerol-1-yl)-2-(*p*-methoxyphenyl)-1,2,3-triazole-5-carboxamide **12b** gave 4-formyl-2-(*p*-methoxyphenyl)-1,2,3-triazole-5-carboxamide **15b** that, on reduction with sodium borohydride, gave the (hydroxymethyl) derivative (**16b**). Similarly, vigorous acetylation of **16b** with boiling acetic anhydride gave the diacetate (**17b**), whereas mild acetylation gave the monoacetyl derivative (**18b**).

On careful 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-(D-*erythro*-glycerol-1-yl)isoxazoline-4,5-dione 4-arylhydrazones (**20**). The infrared spectra of **20** showed a carbonyl absorption at 1725 cm^{-1}, and, in addition, hydroxyl absorption at 3450–3440 cm^{-1} (see Table V).

Treatment of compounds **3** with HBr–HOAc gave 5-*O*-acetyl-6-bromo-6-deoxy-D-*erythro*-2,3-hexodiulosono-1,4-lactone 2-arylhydrazone 3-oximes (**21**). On boiling with acetic anhydride, compounds **21** were cyclized to 4-(2-*O*-acetyl-3-bromo-3-deoxy-D-*erythro*-glycerol-1-yl)-2-aryl-1,2,3-triazole-5-carboxylic acid 5,1[1]-lactones (**22**). The i.r. spectra of **22** showed the lactone band at 1780 cm^{-1}, and the ester band at 1740 cm^{-1}, and the n.m.r. spectra showed one *O*-acetyl-group signal, at δ 2.00–2.02 (see Table VI).



Reaction of **8** and **15** with *o*-phenylenediamine afforded the pyrazoleimidazole, **11** and **19**, respectively; the i.r. spectra showed an NH band at 3200 cm^{-1}, and the amide band at 1680 cm^{-1}.

TABLE I

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

Compound No.	*Ar*	*M.p. (degrees)*	*Molecular formula*	*Analysis*					*ν(cm^{-1})*		
					C	*H*	*Hal.*	*N*	*OH*	*Lactone*	*C=O*
2a	C_6H_4Cl-*p*	208–209[a]									
2b	C_6H_4OMe-*p*	182–183	$C_{13}H_{14}N_2O_6$	Calc.	53.06	4.80		9.52	3450	1725	1680
				Found	53.26	4.61		9.82			
2c	C_6H_4Me-*p*	173–174	$C_{13}H_{14}N_2O_5$	Calc.	56.11	5.07		10.07	3450	1720	1680
				Found	56.32	5.24		9.96			
3a	C_6H_4Cl-*p*	236–237	$C_{12}H_{12}ClN_3O_5$	Calc.	45.94	3.95	11.30	13.38	3450	1730	
				Found	45.59	3.64	11.52	13.50			
3b	C_6H_4OMe-*p*	235–236	$C_{13}H_{15}N_3O_6$	Calc.	50.48	4.89		13.58	3450	1725	
				Found	50.62	4.74		13.32			
3c	C_6H_4Me-*p*	224–226	$C_{13}H_{15}N_3O_5$	Calc.	53.24	5.17		14.33	3450	1720	
				Found	53.24	5.15		14.58			

[a]Lit.[8] m.p. 198–199°.

EXPERIMENTAL

General methods. — Melting points were determined with a Kofler apparatus, and are uncorrected. I.r. spectra were recorded with a Unicam Sp-200 spectrophotometer. Microanalyses were carried out in the Department of Chemistry, Faculty of Science, Cairo University, Cairo, and in the Department of Chemistry, Faculty of Science, Alexandria University, Alexandria. N.m.r. spectra (for solutions in chloroform-*d*), with tetramethylsilane as the standard, were recorded with Varian EM-390 and Cameca spectrometers. Chemical shifts are given on the δ scale. Mass spectra were recorded with an LKB 209 spectrometer; intensities are given in parentheses, as percentages of the base peak.

D-erythro-*2,3-Hexodiulosono-1,4-lactone 2-(arylhydrazones)* (**2**). — A solution of dehydro-D-*arabino*-ascorbic acid (**1**; 0.1 mol) in water (250 mL) was treated with the desired arylhydrazine (0.1 mol) in ethanol (20 mL). The mixture was kept for 3 days at room temperature, and the mono(arylhydrazone) that separated out 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 I.

D-erythro-*2,3-Hexodiulosono-1,4-lactone 2-(arylhydrazone) 3-oximes* (**3**). — A solution of the mono(arylhydrazone) **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 3 h. It was concentrated, and the solid that separated out was filtered off, washed with water, and dried. Each compound was recrystallized from chloroform–ethanol, giving yellow needles. Melting points, formulas, analyses, and i.r. data are listed in Table I.

*2-(*p*-Chlorophenyl)-4-(*D-erythro-*glycerol-1-yl)-1,2,3-triazole-5-carboxylic acid 5,1′-lactone* (**4a**). — A solution of compound **3a** (0.1 g) in water (10 mL) was treated portionwise with bromine (1 mL) in water (10 mL), with stirring. Stirring was continued for 3 h at room temperature, and the excess of bromine was removed by passing a stream of air through the mixture. The product was filtered off, washed with water, and dried (yield, 80 mg). Compound **4a** was recrystallized from ethanol, giving colorless needles; m.p. 195–197°; ν_{max}^{KBr} 3450 (OH) and 1780 cm^{-1} (lactone C=O).

Anal. Calc. for $C_{12}H_{10}ClN_3O_4$: C, 48.74; H, 3.41; Cl, 11.98; N, 14.21. Found: C, 48.71; H, 3.48; Cl, 12.32; N, 14.26.

*2-Aryl-4-(2,3-di-*O*-acetyl-*D-erythro-*glycerol-1-yl)-1,2,3-triazole-5-carboxylic acid 5,1′-lactone* (**5**). — (*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 (see Table II).

(*b*) A suspension of compound **3** (0.1 g) in dry pyridine (5 mL) was treated with acetic anhydride (10 mL), and kept overnight a room temperature. The mixture was poured onto crushed ice, and the product that separated was filtered off,

TABLE II

MICROANALYTICAL AND I.R.-SPECTRAL DATA FOR COMPOUNDS **5–7**

Compound No.	*Ar*	*M.p. (degrees)*	*Molecular formula*	*Analysis*					*ν(cm^{-1})*			
					C	*H*	*Hal.*	*N*	*OH*	*Lactone*	*Ester*	*ONC*
5a	C_6H_4Cl-*p*	79–81	$C_{16}H_{14}ClN_3O_6$	Calc.	50.60	3.71	9.33	11.06		1800	1740	
				Found	50.53	3.54	9.49	11.04				
5b	$C_6H_4OCH_3$-*p*	106–107	$C_{17}H_{17}N_3O_7$	Calc.	54.40	4.57		11.20		1800	1750	
				Found	54.68	4.47		11.54				
5c	$C_6H_4CH_3$-*p*	88–89	$C_{17}H_{17}N_3O_6$	Calc.	56.82	4.76		11.68		1800	1750	
				Found	56.96	4.84		11.64				
6a	C_6H_4Cl-*p*	153–155	$C_{12}H_{14}ClN_5O_4$	Calc.	43.98	4.30		21.36	3450			1680
				Found	43.51	4.31		20.98				
6b	$C_6H_4OCH_3$-*p*	158–160	$C_{13}H_{17}N_5O_5$	Calc.	48.29	5.30		21.66	3400			1680
				Found	48.02	5.41		21.76				
6c	$C_6H_4CH_3$-*p*	140–142	$C_{13}H_{17}N_5O_4$	Calc.	50.81	5.57		22.78	3450			1680
				Found	50.45	5.48		22.32				
6d	C_6H_5	169–170	$C_{12}H_{15}N_5O_4$	Calc.	49.14	5.16		23.88	3450			1680
				Found	49.32	5.22		23.71				
7a	C_6H_4Cl-*p*	112–114	$C_{24}H_{26}ClN_5O_{10}$	Calc.	49.71	4.11	6.11	12.0			1750	1680
				Found	49.26	4.37	6.14	12.10				
7b	$C_6H_4OCH_3$-*p*	141–143	$C_{25}H_{29}N_5O_{11}$	Calc.	52.17	5.08		12.16			1750	1680
				Found	52.36	5.21		12.39				
7c	$C_6H_4CH_3$-*p*	113–115	$C_{25}H_{29}N_5O_{10}$	Calc.	53.67	5.22		12.52			1750	1680
				Found	53.94	5.19		12.43				
7d	C_6H_5	oil	$C_{24}H_{27}N_5O_{10}$	Calc.	52.84	4.99		12.84			1750	1680
				Found	52.49	4.72		12.58				

TABLE III

MICROANALYTICAL AND I R -SPECTRAL DATA FOR COMPOUNDS **8–10**

Compound No.	*Ar*	*M.p. (degrees)*	*Molecular formula*	*Analysis*					$\nu(cm^{-1})$		
					C	*H*	*Hal.*	*N*	*OH*	*Ester*	*ONC*
8a	C_6H_4Cl-*p*	263–265	$C_{10}H_8ClN_5O_2$	Calc.	45.20	3.04	13.35	26.36			1700
				Found	45.36	3.24	13.04	26.39			
8c	$C_6H_4CH_3$-*p*	201–203	$C_{11}H_{11}N_5O_2$	Calc.	53.88	4.52		28.52			1700
				Found	53.49	4.35		28.24			
8d	C_6H_5	192–194	$C_{10}H_9N_5O_2$	Calc.	51.94	3.92		30.29			1690
				Found	51.71	3.72		30.54			
9a	C_6H_4Cl-*p*	152–154	$C_{10}H_{10}ClN_5O_2$	Calc.	44.86	3.76		26.16	3450		1680
				Found	44.62	3.52		26.54			
9c	$C_6H_4CH_3$-*p*	278–280	$C_{11}H_{13}N_5O_2$	Calc.	53.44	5.30		28.31	3450		1680
				Found	53.31	5.24		28.01			
10c	$C_6H_4CH_3$-*p*	>280	$C_{19}H_{21}N_5O_6$	Calc.	54.93	5.10		16.86		1750	1680
				Found	54.64	5.23		16.52			

and recrystallized from ethanol, to give colorless needles identical with those obtained by method (*a*).

(*c*) A suspension of compound **3** (50 mg) in dry pyridine (5 mL) was treated with acetyl chloride (4 mL), and kept overnight at room temperature. The mixture was poured onto crushed ice, and the product was filtered off, and recrystallized from ethanol, giving colorless needles identical with those obtained by method (*a*) or (*b*).

*2-Aryl-4-(*D-erythro-*glycerol-1-yl)-1,2,3-triazole-5-carboxylic acid 5-hydrazides* (**6**). — A solution of compound **5** (0.1 g) in methanol (10 mL) was treated with hydrazine hydrate (1 mL), and kept overnight at room temperature. The solution was concentrated to a small volume, and the solid that separated was filtered off, and dried. The products were recrystallized from ethanol giving colorless needles (see Table II).

Triazole hexaacetates (**7**). — (*a*) A suspension of each compound **6** (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 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 II, and n.m.r. data in Table VI. Mass-spectral data for compound **7d** are given in Table VIII.

(*b*) A solution of each compound **6** (0.1 g) in dry pyridine (5 mL) was treated with acetic anhydride (10 mL), and kept for 3 days at room temperature. The mixture was poured onto crushed ice, and the product that separated was filtered off, successively washed with water and ethanol, and dried. The products were recrystallized from ethanol, affording colorless needles identical with the products obtained by method (*a*).

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

2-Aryl-4-(hydroxymethyl)-1,2,3-triazole-5-carboxylic acid 5-hydrazides (**9**). — A solution of 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 ethanol, to give colorless needles (see Table III).

Triazole tetraacetate (**10**). — A solution of compound **9** (30 mg) in acetic anhydride (10 mL) was boiled under reflux for 1 h. The mixture was cooled, poured onto crushed ice, and the product filtered off, washed with water, and dried. It was recrystallized from ethanol, giving colorless needles (see Table III).

*2-Aryl-4-(*D-erythro-*glycerol-1-yl)-1,2,3-triazole-5-carboxamides* (**12**). — A

TABLE IV

MICROANALYTICAL AND I R -SPECTRAL DATA FOR TRIAZOLECARBOXAMIDES (**12**) AND THEIR ACETATES (**13** AND **14**)

Compound No.	*Ar*	*M.p. (degrees)*	*Molecular formula*	*Analysis*					*ν(cm⁻¹)*		
					C	*H*	*Hal.*	*N*	*OH*	*Ester*	*ONC*
12a	C_6H_4Cl-*p*	188–190	$C_{12}H_{13}ClN_4O_4$	Calc.	46.09	4.19	11.34	17.19	3440		1670
				Found	46.28	4 36	11.56	17.38			
12b	$C_6H_4OCH_3$-*p*	169–171	$C_{13}H_{16}N_4O_5$	Calc.	50.64	5.23		18.18	3450		1680
				Found	50.82	5.41		18.40			
12c	$C_6H_4CH_3$-*p*	187–188	$C_{13}H_{16}N_4O_4$	Calc.	53.42	5.51		19.16	3450		1680
				Found	53.71	5.46		19.38			
12d	C_6H_5	169–171	$C_{12}H_{14}N_4O_4$	Calc.	51.79	5.07		20.14	3450		1680
				Found	51.40	5.42		20.36			
13a	C_6H_4Cl-*p*	132–134	$C_{20}H_{21}ClN_4O_8$	Calc.	49.95	4.40	7.37	11.64		1750	1680
				Found	49.72	4.22	7.52	11.41			
13b	$C_6H_4OCH_3$-*p*	175–177	$C_{21}H_{24}N_4O_9$	Calc.	52.93	5.10		11.76		1750	1680
				Found	52.62	5.37		11.98			
13c	$C_6H_4CH_3$-*p*	144–145	$C_{21}H_{24}N_4O_8$	Calc.	54.78	5.25		12.17		1750	1680
				Found	54.39	5.21		12.48			
14a	C_6H_4Cl-*p*	164–165	$C_{18}H_{19}ClN_4O_7$	Calc.	49.26	4.37	8.07	12.76		1760	1680
				Found	49.36	4.12	8.36	12.41			
14b	$C_6H_4OCH_3$-*p*	160–161	$C_{19}H_{22}N_4O_8$	Calc.	52.53	5.10		12.90		1750	1680
				Found	52.32	5.17		12.57			
14c	$C_6H_4CH_3$-*p*	181–182	$C_{19}H_{22}N_4O_7$	Calc.	54.54	5.30		13.38		1750	1680
				Found	54.73	5 32		13.22			
14d	C_6H_5	118-120	$C_{18}H_{20}N_4O_7$	Calc.	53.46	4.99		13.86		1740	1680
				Found	53.39	4.72		13.61			

solution of each compound **5** (0.1 g) in methanol (10 mL) was treated with concentrated ammonia (10 mL), and kept overnight at room temperature. The solution was concentrated to a small volume, and the solid that separated was filtered off, and dried. The products were recrystallized from ethanol, to give colorless needles (see Table IV).

*2-Aryl-4-(1,2,3-tri-*O*-acetyl-*D*-erythro-glycerol-1-yl)-1,2,3-triazole-5-carboxamides* (**14**). — A solution of each compound **12** (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, washed with water, and dried. Each compound was 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 VI.

Triazole tetraacetates (**13**). — A suspension of each compound **12** (50 mg) 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 was filtered off, washed with water, and dried. The products were recrystallized from ethanol, giving colorless needles. Melting points, formulas, analyses, and i.r. data are listed in Table IV, and n.m.r. data in Table VI.

*4-Formyl-2-(*p*-methoxyphenyl)-1,2,3-triazole-5-carboxamide* (**15b**). — A suspension of compound **12b** (0.1 g) in water (10 mL) was treated with a solution of sodium metaperiodate (0.3 g) in water (10 mL), and the mixture was shaken for 8 h. The solid was filtered off, washed with water, and dried. It was recrystallized from ethanol, giving colorless prisms; m.p. 222–224°; ν_{max}^{KBr} 1690 cm^{-1} (aldehyde + amide).

Anal. Calc. for $C_{11}H_{10}N_4O_3$: C, 53.66; H, 4.09; N, 22.76. Found: C, 53.41; H, 4.32; N, 22.97.

*4-(Hydroxymethyl)-2-(*p*-methoxyphenyl)-1,2,3-triazole-5-carboxamide* (**16b**). — A solution of compound **15b** (0.1 g) in methanol (15 mL) was treated with a solution of sodium borohydride (0.1 g) in water (10 mL), added in a small portions with occasional shaking. The solution was acidified with acetic acid, and the solid was filtered off, washed with water, and dried (yield, 60 mg). It was recrystallized from ethanol, affording colorless needles; m.p. 198–200°; ν_{max}^{KBr} 3450 (OH) and 1680 cm^{-1} (ONC).

Anal. Calc. for $C_{11}H_{12}N_4O_3$: C, 53.22; H, 4.84; N, 22.57. Found: C, 53.57; H, 4.52; N, 22.75.

Triazole diacetate (**17b**). — A suspension of compound **16b** (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 (yield, 50 mg). It was recrystallized from ethanol, to give colorless needles; m.p. 134–135°; ν_{max}^{KBr} 1750 (ester) and 1680 cm^{-1} (ONC); ^{1}H-n.m.r. data ($CDCl_3$): δ 2.14 (s, 3 H, OAc), 2.61 (s, 3 H, NAc), 3.86 (s, 3 H, OMe), 5.53 (s, 2 H, CH_2) and 6.97–7.98 (m, 4 H, C_6H_4).

TABLE V

MICROANALYTICAL AND I.R -SPECTRAL DATA FOR COMPOUND **20–22**

Compound No.	*Ar*	*M.p. (degrees)*	*Molecular formula*	*Analysis*				*ν(cm⁻¹)*		
					C	*H*	*N*	*OH*	*(Lactone +ester)*	*Lactone*
20a	C_6H_4Cl-*p*	142–144	$C_{12}H_{12}ClN_3O_5$	Calc.	45.94	3.85	13.38	3450		1725
				Found	46.22	3.72	13.69			
20d	C_6H_5	148–150	$C_{12}H_{13}N_3O_5$	Calc.	51.61	4.69	15.05	3440		1725
				Found	51.86	4.78	15.34			
21a	C_6H_4Cl-*p*	211–212	$C_{14}H_{13}BrClN_3O_5$	Calc.	40.16	3.13	10.03		1750	
				Found	40.27	3.07	9.72			
21b	$C_6H_4OCH_3$-*p*	193–195	$C_{15}H_{16}BrN_3O_6$	Calc.	43.49	3.89	10.14		1740	
				Found	43.67	3.57	10.48			
21c	$C_6H_4CH_3$-*p*	207–208	$C_{15}H_{16}BrN_3O_5$	Calc.	45.24	4.05	10.54		1750	
				Found	45.41	4.30	10.11			
21d	C_6H_5	198–200	$C_{14}H_{14}BrN_3O_5$	Calc.	43.77	3.67	10.93		1740	
				Found	43.49	3.52	10.71			
22a	C_6H_4Cl-*p*	85–87	$C_{14}H_{11}BrClN_3O_4$	Calc.	41.96	2.76	10.48			1800
				Found	42.31	2.84	10.20			
22c	$C_6H_4CH_3$-*p*	syrup	$C_{15}H_{14}BrN_3O_4$	Calc.	47.38	3.71	11.04			1800
				Found	47.21	3.62	11.36			

TABLE VI

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

Compound	*H-3*	*H-3'*	*H-2*	*H-1*	*Aryl*	*Others*
5a	4.38q	4.56q	5.50q	5.84d	7.50–8.11m	2.04, 2.10 (2s, 2 × 3 H, OAc)
5b	4.34q	4.56q	5.60q	5.80d	7.0 –8.06m	2.03, 2.09 (2s, 2 × 3H, 2 OAc); 3.88 (s, 3 H, OCH_3)
5c	4.40q	4.60q	5.52q	5.81d	7.26–8.02m	2.03, 2.09 (2s, 2 × 3H, 2 OAc); 2.44 (s, 3 H, CH_3)
7a	4.18q	4.39q	5.78q	6.56d	7.26–7.92m	2.05, 2.08, 2.14 (3s, 3 × 3H, 3 OAc); 2.38, 2.45, 2.74 (3s, 3 × 3H, 3 NAc)
7b	4.32q	4.54q	5.62q	5.85d	7.02–8.04m	2.03, 2.06, 2.12 (3s, 3 × 3H, 3 OAc); 2.36, 2.40, 2.44, (3s, 3 × 3H, 3 NAc); 3.86 (s, 3 H, OCH_3)
7c	4.18q	4.38q	5.77q	6.57d	7.26–7.86m	2.05, 2.07, 2.14 (3s, 3 × 3H, 3 OAc); 2.37, 2.41, 2.45, (3s 3 × 3H, 3 NAc); 2.44 (s, 3 H, CH_3)
7d	4.19q	4.40q	5.80q	6.58d	7.44–7.97m	2.05, 2.07, 2.14 (3s, 3 × 3H, 3 OAc); 2.39, 2.46, 2.74, (3 s, 3 × 3H, 3 NAc)
13a	4.18q	4.36q	5.82q	6.74d	7.24–7.94m	2.02, 2.06, 2.14 (3s, 3 × 3H, 3 OAc); 2.36 (s. 3 H, NAc)
13b	4.20q	4.36q	5.76q	6.64d	7.03–7.98m	2.03, 2.06, 2.15 (3s, 3 × 3H, 3 OAc); 2.62 (s, 3 H, NAc); 3.88 (s, 3 H, OCH_3)
13c	4.16q	4,36q	5.80q	6.68d	7.26–7.93m	2.02, 2.06, 2.15 (3s, 3 × 3H, 3 OAc); 2.41 (s, 3 H, CH_3); 2.62 (s, 3 H, NAc)
13d	4.18q	4.35q	5.86q	6.72d	7.22–7.98m	2.02, 2.05, 2.14 (3s, × 3H, 3 OAc); 2.60 (s, 3 H, NAc)
14a	4.20q	4.34q	5.81q	6.71d	7.26–7.97m	2.02, 2.06, 2.15 (3s, 3 × 3H, 3 OAc)
14b	4.19q	4.44q	5.83q	6.74d	7.00–7.97m	2.03, 2.05, 2.15 (3s, 3 × 3H, 3 OAc); 3.86 (s, 3 H, OCH_3)
14c	4.20q	4.40q	5.82q	6.75d	7.28–7.96m	2.03, 2.06, 2.16 (3s, 3 × 3H, 3 OAc); 2.44 (s, 3 H, CH_3)
21a	3.68m		5.73m	5.94d	7.32–7.72m	1.93 (s, 3 H, OAc)
21c	3.62m		5.93m	6.62d	7.13–7.62m	1.93 (s, 3 H, OAc); 2.43 (s, 3 H, CH_3)
22d	3.73m		5.44m	6.04d	7.50–8.12m	2.01 (s, 3 H, OAc)

Anal. Calc. for $C_{15}H_{16}N_4O_5$: C, 54.21; H, 4.85; N, 16.86. Found: C, 54.52; H, 4.72; N, 16.75.

*4-(Acetoxymethyl)-2-(*p*-methoxyphenyl)-1,2,3-triazole-5-carboxamide* (**18b**). — A solution of compound **16b** (50 mg) in 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, washed with water, and dried (yield, 40 mg). It was recrystallized from ethanol, to give colorless needles; m.p. 149–151°; ν_{max}^{KBr} 1750 (ester) and 1680 cm^{-1} (ONC); ^{1}H-n.m.r. data ($CDCl_3$): δ 2.14 (s, 3 H, OAc), 3.86 (s, 3 H, OMe), 5.55 (s, 2 H, CH_2), and 6.97–7.94 (m, 4 H, C_6H_4).

Anal. Calc. for $C_{15}H_{14}N_4O_4$: C, 53.79; H, 4.86; N, 19.30. Found: C, 53.46; H, 4.58; N, 19.57.

*3-(*D-erythro-*glycerol-1-yl)-4,5-isoxazolinedione 4-(phenylhydrazone)* (**20**). — A suspension of each compound **3** (1 mmol) in water (10 mL) was treated with 10% sodium hydroxide solution (20 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 (see Table V). Mass-spectral data for compound **20a** are given in Table X.

*5-O-Acetyl-6-bromo-6-deoxy-*D-erythro-*2,3-hexodiulosono-1,4-lactone 2-(arylhydrazone) 3-oximes* (**21**). — To each compound **3** (0.2 g) was added HBr–HOAc (25 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 with water, and dried. It was recrystallized from ethanol, to give yellow needles (see Table V).

*2-Aryl-4-(2-*O*-acetyl-3-bromo-3-deoxy-*D-erythro-*glycerol-1-yl)-1,2,3-tri-*

TABLE VII

SELECTED IONS IN THE MASS SPECTRUM OF COMPOUND **2c**

Ion	m/z
M + 1	279 (18)
M	278 (100)
M – OH	261 (19)
M – H_2O	260 (100)
M – CH_2O	248 (16)
M – CH_2O – H	247 (68)
M – CH_2O – O	232 (10)
M – CH_2O – OH	231 (66)
M – $2CH_2O$	218 (100)
$CHN_2C_6H_4CH_3$	132 (42)
$N_2C_6H_4CH_3$	119 (100)
$H_2NC_6H_4CH_3$	107 (88)
$NHC_6H_4CH_3$	106 (43)
$C_6H_4CH_3$	91 (50)

TABLE VIII

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

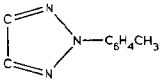
Ion	m/z
M + 1	560 (42)
M	559 (100)
M − CH_2CO + H	518 (12)
M − CH_2CO	517 (31)
M − HOAc + H	500 (40)
M − HOAc	499 (62)
M − 2 CH_2CO	475 (81)
M − 2 CH_2CO − OH	458 (70)
M − 2 CH_2CO − H_2O	457 (90)
M − 3 CH_2CO	433 (10)
M − 3 CH_2CO − OH	416 (32)
M − 3 CH_2CO − H_2O	415 (100)
M − 2 CH_2CO − HOAc − H	414 (72)
M − 3 CH_3CO − HOAc	373 (28)
M − 4 CH_2CO − OH − CH_3 + H	360 (80)
M − 3 CH_2CO − H_2O − HOAc	355 (60)
M − 4 CH_2CO − H_2O − HOAc	313 (42)
	157 (18)
$N_3C_6H_4CH_3$	133 (16)
$N_2C_6H_4CH_3$	119 (21)
$NHC_6H_4CH_3$	106 (32)
$NC_6H_4CH_3$	105 (15)
$C_6H_4CH_3$	91 (90)

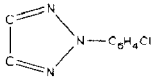
TABLE IX

SELECTED IONS IN THE MASS SPECTRUM OF COMPOUND **13c**

Ion	m/z
M + 1	461 (23)
M	460 (100)
M − CH_2CO + H	419 (18)
M − Me − CH_2CO	403 (16)
M − HOAc + H	401 (47)
M − HOAc	400 (13)
M − HOAc − OH	383 (76)
M − HOAc − H_2O	382 (64)
M − 2 CH_2CO	376 (21)
M − 2 CH_2CO − H_2O	358 (92)
M − 3 CH_2CO − OH	317 (24)
M − 4 CH_2CO + 2 H	294 (34)
$N_3C_6H_4Me$	133 (56)
$N_2C_6H_4Me$	119 (32)
NC_6H_4Me	104 (21)
C_6H_4Me	91 (67)

TABLE X

SELECTED IONS IN THE MASS SPECTRUM OF COMPOUND **20a**

Ion	m/z
M + 1	337 (54); 339 (26)
M	336 (82); 338 (42)
M − CH_2CO	294 (100); 296 (32)
M − Cl − CH_2CO	259 (36)
M − 2 CH_2CO	252 (46); 254 (40)
M − 2 CH_2CO − Cl	217 (13)
	178 (32); 180 (20)
$N_3C_6H_4Cl$	153 (14); 155 (8)
$N_2C_6H_4Cl$	139 (30); 141 (10)
HNC_6H_4Cl	126 (12); 128 (6)
NC_6H_4Cl	125 (18); 127 (12)
C_6H_4Cl	111 (72); 113 (32)

azole-5-carboxylic acid 5,1′-lactone (**22**). — A suspension of compound **21** (0.1 g) in acetic anhydride (5 mL) was boiled under reflux for 30 min. The mixture was poured onto crushed ice, and the product was filtered off, washed with water, and dried. It was recrystallized from ethanol, giving colorless needles (see Table V).

Triazoleimidazole (**11c**). — A solution of compound **8c** (20 mg) in methanol was treated with *o*-phenylenediamine (30 mg) in methanol (20 mL) containing a few drops of acetic acid. The mixture was boiled under reflux for 3 h, and cooled to room temperature, and the solid was filtered off, washed with ether, and dried. Compound **11c** was recrystallized from ethanol, to give red needles; m.p. >280°; ν_{max}^{KBr} 3200 (NH) and 1680 $^{-1}$ (ONC).

Anal. Calc. for $C_{17}H_{17}N_7O$: C, 60.88; H, 5.11. Found: C, 60.53; H, 5.32.

Triazoleimidazole (**19b**). — This compound was prepared as described for compound **11c**; m.p. >280°; ν_{max}^{KBr} 3200 (NH) and 1680 cm^{-1} (ONC).

Anal. Calc. for $C_{17}H_{16}N_6O_2$: C, 60.70; H, 4.80. Found: C, 60.43; H, 4.58.

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