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STUDIES ON DEHYDRO-L-ASCORBIC ACID 3-OXIME 2-PHENYLHYDRAZONE: CONVERSION INTO SUBSTITUTED TRIAZOLES*

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ABSTRACT

L-*threo*-2,3-Hexodiulosono-1,4-lactone 3-oxime 2-(phenylhydrazone) (**1**) gave 2-(*p*-bromophenyl)-4-(L-*threo*-1,2,3-trihydroxypropyl)-1,2,3-triazole-5-carboxylic acid 5,1[1]-lactone (**2**), and this gave a diacetyl and a dibenzoyl derivative. On treatment of **2** with liquid ammonia, methylamine, or dimethylamine, the corresponding triazole-5-carboxamides (**5–7**) were obtained. Periodate oxidation of **5** gave 2-(*p*-bromophenyl)-4-formyl-1,2,3-triazole-5-carboxamide (**10**), and, on reduction, **10** gave 2-(*p*-bromophenyl)-4-(hydroxymethyl)-1,2,3-triazole-5-carboxamide, characterized as its monoacetate. Condensation of **10** with phenylhydrazine gave the triazole hydrazone. Acetonation of **2** gave the isopropylidene derivative. Reaction of **2** with HBr–HOAc gave 4-(L-*threo*-2-*O*-acetyl-3-bromo-1,2-dihydroxypropyl)-2-(*p*-bromophenyl)-1,2,3-triazole-5-carboxylic acid 5,1[1]-lactone. Similar treatment of **1** with HBr–HOAc gave 5-*O*-acetyl-6-bromo-6-deoxy-L-*threo*-2,3-hexodiulosono-1,4-lactone 3-oxime 2-(phenylhydrazone). This was converted into 4-(L-*threo*-2-*O*-acetyl-3-bromo-1,2-dihydroxypropyl)-2-phenyl-1,2,3-triazole-5-carboxylic acid 5,1[1]-lactone on treatment with boiling acetic anhydride. On reaction of **1** with benzoyl chloride in pyridine, dehydrative cyclization occurred, with the formation of 4-(L-*threo*-2,3-dibenzoyloxy-1-hydroxypropyl)-2-phenyl-1,2,3-triazole-5-carboxylic acid 5,1[1]-lactone, which was converted into the amide on treatment with ammonia.

DISCUSSION

In continuation of our work on the synthesis of nitrogen heterocycles from dehydro-L-ascorbic acid bis(hydrazone)s[2–5] and analogs[1,6,7], we now describe the synthesis and some reactions of 2-(*p*-bromophenyl)-, as well as the bromodeoxy-, triazole derivatives prepared from dehydro-L-ascorbic acid 3-oxime 2-(phenylhydrazone)[8]. Thus, reaction of dehydro-L-ascorbic acid 3-oxime 2-(phenylhydrazone) [L-*threo*-2,3-hexodiulosono-1,4-lactone 3-oxime 2-(phenylhydrazone)] (**1**) with bromine water caused its dehydrative cyclization, to give 2-(*p*-bromophenyl)-4-(L-*threo*-1,2,3-trihydroxypropyl)-1,2,3-triazole-5-carboxylic acid 5,1[1]-lactone (**2**); this

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

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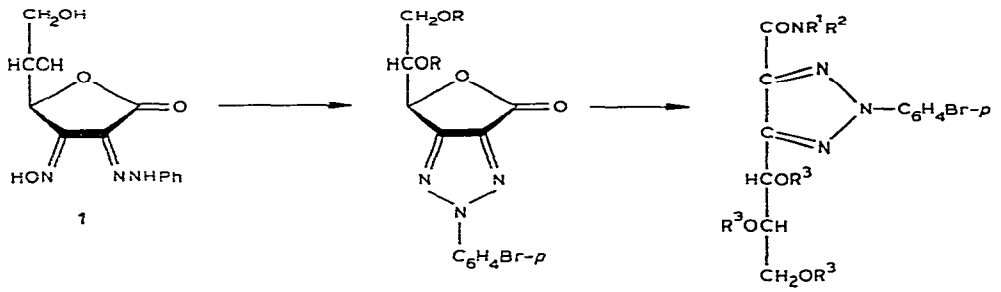
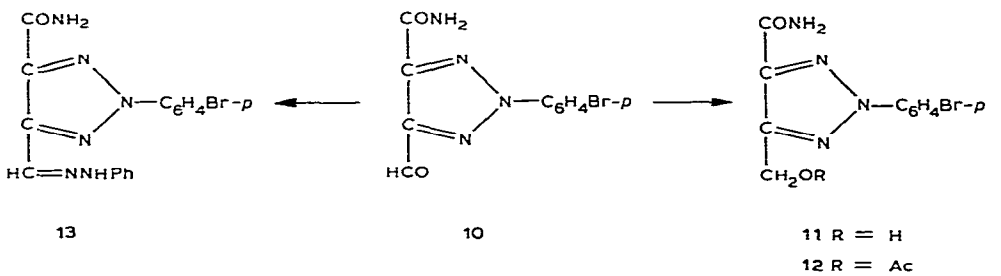




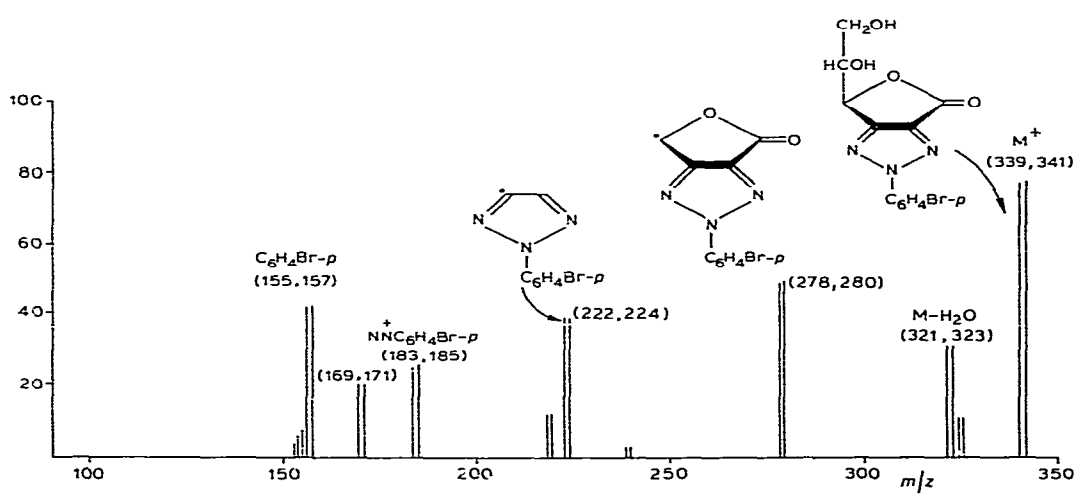


Fig. 1. Mass spectrum of compound 2.

reaction is similar to that conducted[1] on the 5-epimer of **1**. The mass spectrum of **2** (Fig. 1) showed the molecular-ion peak at *m/z* 339,341, which is the base peak; it appears as two peaks having almost the same intensity owing to the equal abundance of the two isotopes of bromine. This was followed by a peak at *m/z* 321,323 resulting from the elimination of a molecule of water from the side chain, and a fragment at *m/z* 278,280, due to the loss of the side chain.

Acetylation of compound **2** with boiling acetic anhydride, or with acetic anhydride and pyridine, gave 2-(*p*-bromophenyl)-4-(L-*threo*-2,3-diacetoxy-1-hydroxypropyl)-1,2,3-triazole-5-carboxylic acid 5,1[1]-lactone (**3**). The n.m.r. spectrum of **3** showed two singlets, of three-proton intensity each, at δ 2.02 and 2.08 (two acetyl groups), two protons centered at δ 4.41 (due to the methylene group at C-3), a multiplet at δ 5.48 assigned to the C-2 methine proton, and a doublet at δ 5.85 (J 2 Hz) due to the C-1 methine proton. The protons of the phenyl group appeared at δ 7.5–8.0 as a multiplet of four-proton intensity. Similar treatment of **2** with benzoyl chloride and pyridine afforded the di-*O*-benzoyl derivative (**4**).

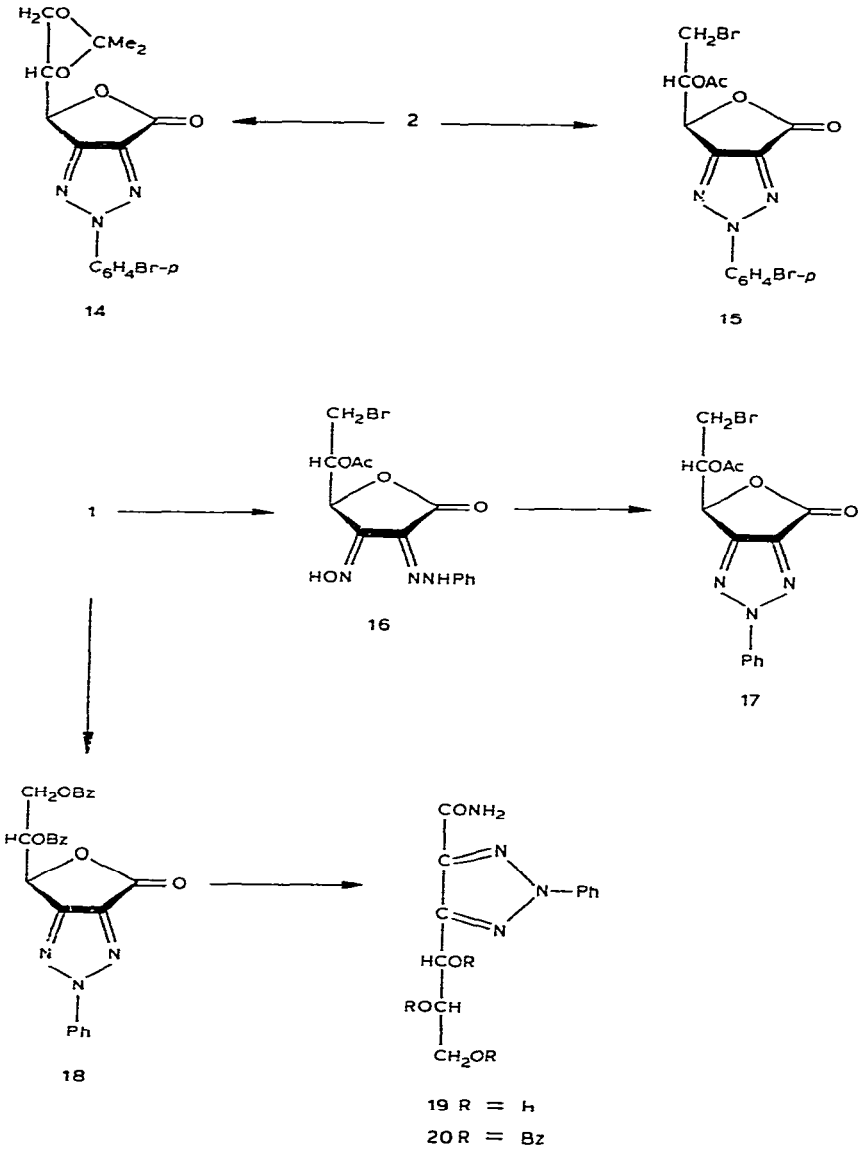
On treatment of compound **2** with liquid ammonia, methylamine, or dimethylamine, opening of the lactone ring occurred, yielding compounds **5**–**7**. The infrared spectra of compounds **5**–**7** showed the amide band at 1690–1670 cm^{-1}, in addition to the hydroxyl band at 3500–3450 cm^{-1}; the lactone band of the starting compound **2** (at 1780 cm^{-1}) had disappeared. Acetylation of **5** with boiling acetic anhydride afforded a triacetate designated 2-(*p*-bromophenyl)-4-(L-*threo*-1,2,3-triacetoxypropyl)-1,2,3-triazole-5-carboxamide (**8**). Similarly, benzoylation of **5** afforded the tri-*O*-benzoyl derivative (**9**).

Periodate oxidation of one mole of **5** resulted in the consumption of two moles of the oxidant, with the formation of 2-(*p*-bromophenyl)-4-formyl-1,2,3-triazole-5-carboxamide (**10**); the infrared spectrum of **10** showed a band at 1700 cm^{-1} due to the aldehyde group, in addition to an amide band at 1690 cm^{-1}, and there was no hydroxyl absorption.

Reduction of **10** with sodium borohydride afforded 2-(*p*-bromophenyl)-4-(hydroxymethyl)-1,2,3-triazole-5-carboxamide (**11**), characterized as its acetate (**12**). On condensation of **10** with phenylhydrazine, 2-(*p*-bromophenyl)-3-formyl-1,2,3-triazole-5-carboxamide 3-(phenylhydrazone) (**13**) was obtained. Reaction of **2** with acetone afforded the isopropylidene derivative (**14**).

Treatment of **2** with hydrogen bromide in acetic acid gave 4-(L-*threo*-2-acetoxy-3-bromo-1-hydroxypropyl)-2-(*p*-bromophenyl)-1,2,3-triazole-5-carboxylic acid 5,1[1]-lactone (**15**); its infrared spectrum showed the lactone band at 1780 cm^{-1} and the ester band at 1720 cm^{-1}. The n.m.r. spectrum of **15** in chloroform-*d* showed one acetyl group, at δ 2.08, a methylene group centered at δ 4.38, a multiplet at δ 5.38 (the C-2 methine proton), and a doublet at δ 5.96 (J 3 Hz) due to the C-1 methine proton; the phenyl group appeared at δ 7.4–7.9.

5-*O*-Acetyl-6-bromo-6-deoxy-L-ascorbic acid has been prepared from L-ascorbic acid by treatment with hydrogen bromide in acetic acid[9,10]. Similar treatment of **1** with HBr–HOAc gave 5-*O*-acetyl-6-bromo-6-deoxy-L-*threo*-2,3-hexodiulosono-



1,4-lactone 3-oxime 2-(phenylhydrazone) (**16**), as shown by its elemental analysis, which agreed with that calculated for the molecular formula $C_{14}H_{14}BrN_3O_5$, corresponding to **16**; its infrared spectrum showed the lactone and ester band at 1750 cm^{-1}, in addition to the hydroxyl band at 3350 cm^{-1}. On boiling with acetic anhydride, compound **16** was dehydratively cyclized to 4-(L-*threo*-2-acetoxy-3-bromo-1-hydroxypropyl)-2-phenyl-1,2,3-triazole-5-carboxylic acid 5,1^1-lactone (**17**). The n.m.r. spectrum of **17** in chloroform-*d* showed one acetyl group, at δ 2.0, a multiplet centered at δ 3.64 attributed to the C-3 methylene group, a multiplet at δ 5.40 of

TABLE I

MICROANALYTICAL AND SPECTRAL DATA FOR 2-(*p*-BROMOPHENYL)-4-(L-*threo*-1,2,3-TRIHYDROXYPROPYL)-1,2,3-TRIAZOLE-5-CARBOXAMIDE (**5**) AND ITS DERIVATIVES (**6**, **7**)

Compound No.	R_1	R_2	*M.p. (degrees)*	*Molecular formula*	*Analysis*	*C*	*H*	*Br*	*N*	*ν (cm⁻¹) OH*	*CON*
5	H	H	148–149	$C_{12}H_{13}BrN_4O_4$	Calc.	40.32	3.64	22.37	15.68	3450	1680
					Found	40.06	3.40	22.69	15.47		
6	H	Me	188–189	$C_{13}H_{15}BrN_4O_4$	Calc.	42.06	4.07		15.08	3450	1690
					Found	42.40	4.36		15.23		
7	Me	Me	128–129	$C_{14}H_{17}BrN_4O_4$	Calc.	43.65	4.45	20.74	14.54	3450	1690
					Found	43.32	4.61	20.46	14.20		

one-proton intensity due to the adjacent C-2 proton, and a doublet at δ 5.96 (J 3 Hz) due to the C-1 proton; the phenyl protons appeared at δ 7.30–8.15.

Reaction of **1** with benzoyl chloride and pyridine gave 4-(L-*threo*-2,3-dibenzoyloxy-1-hydroxypropyl)-2-phenyl-1,2,3-triazole-5-carboxylic acid 5,1[1]-lactone (**18**), and, on treatment with ammonia, this gave 2-phenyl-4-(L-*threo*-1,2,3-trihydroxypropyl)-1,2,3-triazole 5-carboxamide[8] (**19**), characterized as its benzoyl derivative (**20**).

EXPERIMENTAL

General methods. — Melting points were determined on a Kofler-block apparatus and are uncorrected. I.r. spectra were recorded with a Unicam Sp-1025 spectrophotometer for potassium bromide pellets. Microanalyses were performed in the Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt. N.m.r. and mass spectra were recorded with a Varian EM-390 and M 60 spectrometer, respectively.

L-threo-*2,3-Hexodiulosono-1,4-lactone 3-oxime 2-(phenylhydrazone)*[8] (**1**). — A solution of L-*threo*-2,3-hexodiulosono-1,4-lactone 2-(phenylhydrazone)[11,12] (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 2 h. It was then concentrated, water (10 mL) was added, and the solid that separated was filtered off, washed successively with water, ethanol, and ether, and dried (yield 0.8 g). Compound **1** was recrystallized from ethanol, giving yellow needles, m.p. 224–226° (lit.[8] m.p. 224–226°).

2-(p-*Bromophenyl*)-*4*-(L-threo-*1,2,3-trihydroxypropyl*)-*1,2,3-triazole-5-carboxylic acid 5,1*[1]*-lactone* (**2**). — A solution of compound **1** (1 g) in water (20 mL) was treated portionwise with bromine (2 mL) in water (10 mL) with stirring. Stirring was continued for 12 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, succes-

sively washed with water, ethanol, and ether, and dried (yield 0.6 g). Compound **2** was recrystallized from ethanol, to give colorless needles, m.p. 155–156°; ν_{max}^{KBr} 3450 (OH) and 1780 cm^{-1} (lactone C=O).

Anal. Calc. for $C_{12}H_{10}BrN_3O_4$: C, 42.37; H, 2.96; Br, 23.49; N, 12.35. Found: C, 42.26; H, 3.12; Br, 23.16; N, 12.18.

*2-(p-Bromophenyl)-4-(*L-threo-*2,3-diacetoxy-1-hydroxypropyl)-1,2,3-triazole-5-carboxylic acid 5,1¹-lactone* (**3**). — (*a*). A suspension of compound **2** (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 (yield 70 mg). Compound **3** was recrystallized from ethanol, giving colorless needles, m.p. 136–137°; ν_{max}^{KBr} 1780 (lactone C=O), 1740 (ester), and 1600 cm^{-1} (C=N). It is soluble in acetone or chloroform, sparingly soluble in methanol or ethanol, and insoluble in water.

Anal. Calc. for $C_{16}H_{14}BrN_3O_6$: C, 45.30; H, 3.33; Br, 18.83; N, 9.90. Found: C, 45.56; H, 3.52; Br, 18.97; N, 10.16.

(*b*). A solution of compound **2** (0.1 g) in dry pyridine (10 mL) was treated with acetic anhydride (10 mL), and the mixture was kept overnight at room temperature, and poured onto crushed ice; the solid was filtered off, successively washed with water and ethanol, and dried (yield 50 mg). Compound **3** was recrystallized from ethanol, giving colorless needles, m.p. 136–137°, alone or admixed with the product from (*a*). The two products had identical i.r. and n.m.r. spectra.

*2-(*p-*Bromophenyl)-4-(*L-threo-*2,3-dibenzoyloxy-1-hydroxypropyl)-1,2,3-triazole-5-carboxylic acid 5,1¹-lactone* (**4**). — A solution of compound **2** (0.1 g) in dry pyridine (10 mL) was treated with benzoyl chloride (0.1 mL), and kept overnight at room temperature. The mixture was poured onto crushed ice, and the product was filtered off, successively washed with water and ethanol, and dried (yield 30 mg). Compound **4** was recrystallized from ethanol, giving colorless needles, m.p. 145–146°; ν_{max}^{KBr} 1750 cm^{-1} (lactone C=O, and ester).

Anal. Calc. for $C_{26}H_{18}BrN_3O_6$: C, 56.95; H, 3.31; Br, 14.57; N, 7.66. Found: C, 56.72; H, 3.62; Br, 14.86; N, 7.41.

*2-(*p-*Bromophenyl)-4-(*L-threo-*1,2,3-trihydroxypropyl)-1,2,3-triazole-5-carboxamide and its derivatives* (**5–7**). — A solution of **2** (0.1 g) in methanol (10 mL) was treated respectively with ammonia, methylamine, or dimethylamine (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–water in colorless needles. Melting points, formulas, analyses, and spectral data are listed in Table I.

*2-(*p-*Bromophenyl)-4-(*L-threo-*1,2,3-triacetoxypropyl)-1,2,3-triazole-5-carboxamide* (**8**). — A suspension of **5** (0.1 g) in acetic anhydride (10 mL) was boiled under reflux for 30 min, cooled, and poured onto crushed ice. Compound **8** was obtained as a syrup; ^{1}H-n.m.r. data ($CDCl_3$): δ 6.5 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 6.0 (m, 1 H, H-2), 4.33 (m, 2 H, H-3), 2.03, 2.09, and 2.12 (9 H, 3 $OCOCH_3$), 7.16 (m, 2 H, NH_2), and 7.2–8.1 (m, 4 H, phenyl); ν_{max}^{Nujol} 1730 (ester) and 1690 cm^{-1} (CON).

Anal. Calc. for $C_{18}H_{19}BrN_4O_7$: C, 44.73; H, 3.96; N, 11.58. Found: C, 44.36; H, 4.12; N, 11.42.

2-(p-Bromophenyl)-4-(L-threo-1,2,3-tribenzoyloxypropyl)-1,2,3-triazole-5-carboxamide (**9**). — A solution of compound **5** (0.1 g) in dry pyridine (10 mL) was treated with benzoyl chloride (0.2 mL), and kept overnight at room temperature. The mixture was poured onto crushed ice, and the product was filtered off, successively washed with water and ethanol, and dried (yield 40 mg). Compound **9** was recrystallized from ethanol, giving colorless prisms, m.p. 188–190°; ν_{max}^{KBr} 1730 (ester) and 1680 cm^{-1} (CON).

Anal. Calc. for $C_{33}H_{25}BrN_4O_7$: C, 59.20; H, 3.76; Br, 11.93. Found: C, 59.46; H, 3.39; Br, 11.71.

2-(p-Bromophenyl)-4-formyl-1,2,3-triazole-5-carboxamide (**10**). — A suspension of compound **5** (0.1 g) in water (20 mL) was treated with a solution of sodium metaperiodate (0.5 g) in water (10 mL), and the mixture was shaken for 4 h. The solid was filtered off, washed with water, and dried (yield 30 mg). It was recrystallized from ethanol, to give colorless plates, m.p. 250–252°; ν_{max}^{KBr} 1700 (CHO) and 1690 cm^{-1} (CON).

Anal. Calc. for $C_{10}H_7BrN_4O_2$: C, 40.70; H, 2.39; Br, 27.08; N, 18.97. Found: C, 40.32; H, 2.46; Br, 27.35; N, 18.62.

2-(p-Bromophenyl)-4-(hydroxymethyl)-1,2,3-triazole-5-carboxamide (**11**). — A solution of compound **10** (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 (yield 60 mg). Compound **11** was recrystallized from ethanol, giving colorless prisms, m.p. 234–235°; ν_{max}^{KBr} 3450 (OH) and 1690 cm^{-1} (CON).

Anal. Calc. for $C_{10}H_9BrN_4O_2$: C, 40.43; H, 3.05; N, 18.85. Found: C, 40.72; H, 3.24; N, 18.61.

4-(Acetoxymethyl)-2-(p-bromophenyl)-1,2,3-triazole-5-carboxamide (**12**). — A solution of compound **11** (60 mg) 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, successively washed with water and ethanol, and dried (yield 40 mg). Recrystallization from chloroform–ethanol gave compound **12** as colorless prisms, m.p. 182–183°; ^{1}H-n.m.r. data ($CDCl_3$): δ 4.86 (s, 2 H, H-1), 2.08 (s, 3 H, $OCOCH_3$), and 7.46–7.92 (m, 4 H, phenyl); ν_{max}^{KBr} 1720 (OAc) and 1680 cm^{-1} (CON).

Anal. Calc. for $C_{12}H_{11}BrN_4O_3$: C, 42.50; H, 3.26; Br, 23.56; N, 16.51. Found: C, 42.76; H, 3.02; Br, 23.19; N, 16.28.

2-(p-Bromophenyl)-3-formyl-1,2,3-triazole-5-carboxamide 3-phenylhydrazone (**13**). — To a solution of **10** (0.1 g) in ethanol (10 mL) was added phenylhydrazine (0.1 mL) in ethanol (10 mL) and few drops of acetic acid, and the solution was boiled under reflux for 2 h. The solid that separated on cooling was filtered off and dried (yield 40 mg). It was recrystallized from ethanol, to give pale-yellow needles, m.p. 220–222°; ν_{max}^{KBr} 1690 cm^{-1} (CON).

Anal. Calc. for $C_{16}H_{13}BrN_6O$: C, 49.89; H, 3.40; N, 21.81. Found: C, 49.63; H, 3.52; N, 21.54.

*2-(p-Bromophenyl)-4-(*L-threo-*2,3-O-isopropylidene-1,2,3-trihydroxypropyl)-1,2,3-triazole-5-carboxylic acid 5,1¹-lactone* (**14**). — A solution of compound **2** (0.1 g) in dry acetone (10 mL) was treated with two drops of concentrated sulfuric acid and kept for 24 h at room temperature. The solution was evaporated under diminished pressure to a thin syrup, water (10 mL) was added, and the solid was filtered off, and dried (yield 50 mg). Recrystallization from ethanol–benzene gave compound **14** as colorless prisms, m.p. 187–188°; ν_{max}^{KBr} 1770 cm^{-1} (lactone C=O).

Anal. Calc. for $C_{15}H_{14}BrN_3O_4$: C, 47.38; H, 3.71; N, 11.04. Found: C, 47.08; H, 3.46; N, 10.89.

*4-(*L-threo-*2-Acetoxy-3-bromo-1-hydroxypropyl)-2-(*p-*bromophenyl)-1,2,3-triazole-5-carboxylic acid 5,1¹-lactone* (**15**). — To compound **2** (0.1 g) was added HBr–HOAc (20 mL), and the mixture was stirred for 30 h at room temperature. Water (50 mL) was added, and the solid that separated was filtered off, washed successively with water, ethanol, and ether, and dried (yield 60 mg). Compound **15** was recrystallized from ethanol, giving colorless prisms, m.p. 108–109°; ν_{max}^{KBr} 1780 (lactone C=O), 1720 (OAc), and 1600 cm^{-1} (C=N).

Anal. Calc. for $C_{14}H_{11}Br_2N_3O_4$: C, 37.78; H, 2.49; Br, 35.90; N, 9.43. Found: C, 37.34; H, 2.38; Br, 36.20; N, 9.12.

*5-O-Acetyl-6-bromo-6-deoxy-*L-threo-*2,3-hexodiulosono-1,4-lactone 3-oxime 2-(phenylhydrazone)* (**16**). — To compound **1** (1 g) was added HBr–HOAc (20 mL), and the mixture was stirred for 24 h at room temperature. Water (50 mL) was added, and the solid that separated was filtered off, washed successively with water, ethanol, and ether, and dried (yield 0.9 g). Compound **16** was recrystallized from chloroform–ethanol, giving yellow needles, m.p. 214–215°; ν_{max}^{KBr} 3350 (OH) and 1750 cm^{-1} (lactone C=O + OAc); λ_{max}^{EtOH} 226, 286, and 378 nm (log ε 4.00, 3.56, and 4.42), λ_{min}^{EtOH} 262 and 300 nm (log ε 3.41 and 3.32).

Anal. Calc. for $C_{14}H_{14}BrN_3O_5$: C, 43.77; H, 3.67; Br, 20.79; N, 10.93. Found: C, 43.70; H, 3.70; Br, 20.73; N, 10.70.

*4-(*L-threo-*2-Acetoxy-3-bromo-1-hydroxypropyl)-2-phenyl-1,2,3-triazole-5-carboxylic acid 5,1¹-lactone* (**17**). — A solution of compound **16** (0.1 g) in dry pyridine (10 mL) was treated with acetic anhydride (5 mL), and kept for 24 h 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 (yield 40 mg). Compound **17** was recrystallized from ethanol, giving colorless needles, m.p. 129–130°; ν_{max}^{KBr} 1800 (lactone C=O) and 1760 cm^{-1} (OAc).

Anal. Calc. for $C_{14}H_{12}BrN_3O_4$: C, 45.92; H, 3.30; Br, 21.82; N, 11.47. Found: C, 46.06; H, 3.45; Br, 21.71; N, 11.62.

*4-(*L-threo-*2,3-Dibenzoyloxy-1-hydroxypropyl)-2-phenyl-1,2,3-triazole-5-carboxylic acid 5,1¹-lactone* (**18**). — A suspension of compound **1** (1 g) in dry pyridine (10 mL) was treated with benzoyl chloride (1 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 0.2 g). Compound **18** was recrystallized from ethanol, to give colorless needles, m.p. 74–75°; ν_{max}^{KBr} 1760 (lactone C=O + OBz) and 1600 cm^{-1} (C=N).

Anal. Calc. for $C_{26}H_{19}N_3O_6$: C, 66.52; H, 4.08; N, 8.95. Found: C, 66.74; H, 4.18; N, 8.85.

2-Phenyl-4-(L-threo-*1,2,3-trihydroxypropyl*)-*1,2,3-triazole-5-carboxamide* (**19**). — A solution of compound **18** (0.1 g) in methanol (10 mL) was treated with liquid ammonia (10 mL), and kept overnight at room temperature. The solution was concentrated under diminished pressure, and the solid that separated was filtered off and dried (yield 80 mg). Compound **19** was recrystallized from ethanol, giving colorless needles: m.p. 184–185° (lit.[8] m.p. 184–185°).

2-Phenyl-4-(L-threo-*1,2,3-tribenzoyloxypropyl*)-*1,2,3-triazole-5-carboxamide* (**20**). — A solution of **19** (0.1 g) in dry pyridine (10 mL) was treated with benzoyl chloride (0.1 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 70 mg). Compound **20** was recrystallized from ethanol, to give colorless needles, m.p. 116–117°; ν_{max}^{KBr} 1730 (ester) and 1690 cm^{-1} (CON).

Anal. Calc. for $C_{33}H_{26}N_4O_7$: C, 67.11; H, 4.43; N, 9.48. Found: C, 66.83; H, 4.54; N, 9.16.

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