HETEROCYCLES FROM CARBOHYDRATE PRECURSORS
STUDIES ON DEHYDRO-D-erythroASCORBIC ACID 2-ARYLHYDRAZONE 3-OXIMES: CONVERSION INTO SUBSTITUTED TRIAZOLES AND ISOXAZOLINES

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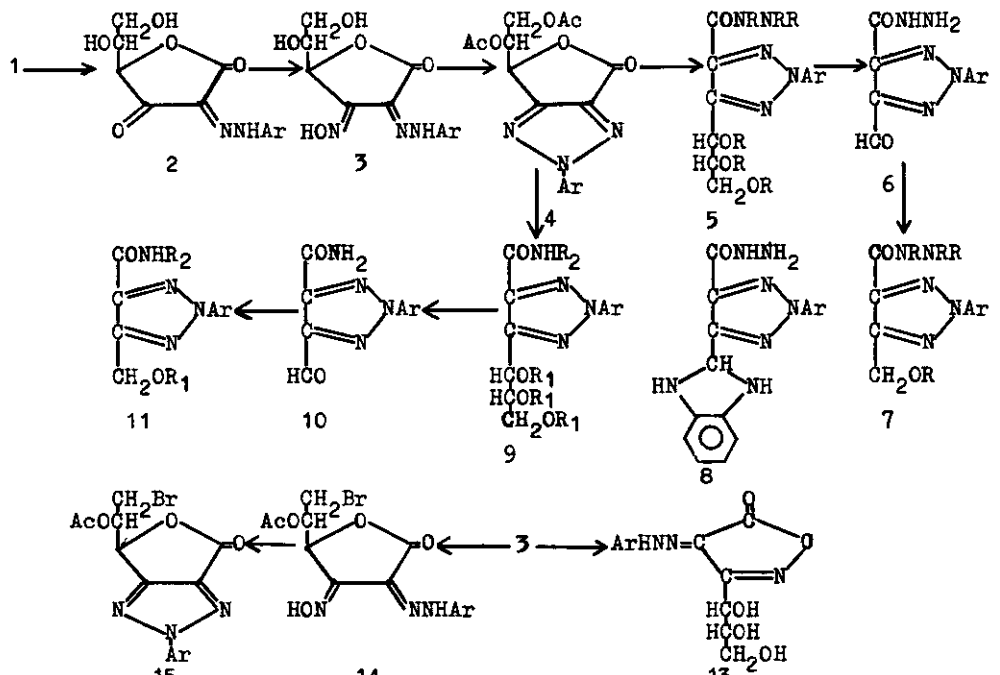
D-erythro-2,3-Hexodiulosono-1,4-lactone 2-arylhydrazones (2) were prepared by condensation of dehydro-D-erythroascorbic acid (1) with the desired arylhydrazine. Reaction of 2 with hydroxylamine, gave the 2-arylhydrazone 3-oximes (3). On boiling with acetic anhydride 3, gave 2-aryl-4-(di-O-acetyl-D-erythro-glycerol-1-yl)-1,2,3-triazole-5-carboxylic acid 5,1'-lactone (4). On treatment of 4 with hydrazine hydrate, 2-aryl-4-(D-erythro-1,2,3-trihydroxypropyl)-1,2,3-triazole 5-hydrazides (5,R=H) were obtained. Acetylation of 5 gave the hexaacetyl derivatives (5,R=Ac). Similarly, treatment of 4 with liquid ammonia, gave the triazole carboxamides (9,R_1=R_2=H). Vigorous acetylation of 9 with boiling acetic anhydride, gave the tetraacetates (9,R_1=R_2=Ac), while acetylation of 9 with acetic anhydride-pyridine, gave the triacetates (9,R_1=Ac,R_2=H), Periodate oxidation of 5 gave the 2-aryl-4-formyl-1,2,3-triazole 5-hydrazides (6), and, on reduction, 6 gave the 2-aryl-4-hydroxymethyl-1,2,3-triazole 5-hydrazides (7,R=H) characterized as their acetates (7,R=Ac). Similarly, periodate oxidation of 9 gave the triazole aldehyde (10) that on reduction of 10 gave the hydroxymethyl derivative (11,R_1=R_2=H). Acetylation of 11 gave the mono- and diacetates, and reaction of 6 with o-phenylenediamine, afforded the triazole imidazole (8). Controlled reaction of 3 with sodium hydroxide followed by nutralization, gave 3-(D-erythro-1,2,3-trihydroxypropyl)-4,5-isoxazolinedione 4-arylhydrazones (13). Reaction of 3 with HBr-HOAc, gave 5-O-acetyl-6-bromo-6-deoxy-D-erythro-2,3-hexodiulosono-1,4-lactone 2-arylhydrazones 3-oximes14. 14 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'-lactone on treatment with acetic anhydride



(a) Ar=C_6H_4Cl-p; (b) Ar=$C_6H_4CH_3$-p; (c) Ar=$C_6H_4OCH_3$-p (d) Ar=Ph