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## Sugar Lactams. II. 4-Amino-4-deoxy-D-erythrulactam and Related Products

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Sir:

In the preceding communication (1), the synthesis of a six-membered sugar lactam, in which the nitrogen atom was part of the ring system, was described. We now report the synthesis of another novel carbohydrate of the same class, namely, 4-amino-4-deoxy-D-erythrulactam (V) which is a sugar containing the nitrogen function in a five-membered ring.

This synthesis has brought forward a new route to aminosugars which involves the reaction of sugar lactones with sodium azide in dimethyl sulfoxide or dimethylformamide to give azido aldonic acids. Such derivatives could be readily converted to azido aldoses and hence to hitherto inaccessible amino-sugars. This communication describes the synthesis of an  $\omega$ -azido aldonic acid and some of its derivatives. The reaction of lactones formed from primary alcoholic groups and carboxyl groups, with sodium azide has been recently described (2).

Treatment of 2,4-O-ethylidene-D-erythrose (3) (crystalline dimer) with perpropionic acid gave crystalline D-erythrulactone (3) which was converted to 2,3-O-isopropylidene-D-erythrulactone (I) according to Mitchell (4). The latter was allowed to react with sodium azide in dimethyl sulfoxide at 110° overnight in an atmosphere of nitrogen to give crystalline 4-azido-4-deoxy-2,3-O-isopropylidene-D-erythronic acid (II), m.p. 55-6°;  $[\alpha]_D^{25} +72^\circ$  (c., 0.47 in acetone);  $\lambda$  max 2000  $\text{cm}^{-1}$  ( $\text{N}_3$ ); 1760  $\text{cm}^{-1}$  (C=O) (Calcd. for  $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_4$ : C, 41.80; H, 5.51; N, 20.90. Found: C, 42.20; H, 5.87; N, 21.08) (5).

Reduction of II with hydrogen over Pd-C at room temperature and atmospheric pressure afforded crystalline 4-amino-4-deoxy-2,3-O-isopropylidene-D-erythronic acid (III), m.p. 150-160° (sublimes),  $[\alpha]_D^{25} +92^\circ$  (c., 1.02 in 60% aq. acetone) (Calcd. for  $\text{C}_7\text{H}_{13}\text{NO}_4 \cdot \text{H}_2\text{O}$ : C, 43.51; H, 7.83; N, 7.25. Found: C, 43.51; H, 7.93; N, 7.16). The infrared spectrum showed evidence of the presence of a zwitter ion (6). The amino acid III gave a positive test with ninhydrin. Sublimation of III at 150° and 0.5 mm. afforded crystalline 4-amino-4-deoxy-2,3-O-isopropylidene-D-erythrulactam (IV), m.p. 147-8°,  $[\alpha]_D^{25} -59^\circ$  (c., 0.78 in MeOH) (Calcd. for  $\text{C}_7\text{H}_{11}\text{NO}_3 \cdot 1/2\text{H}_2\text{O}$ : C, 50.59; H, 7.28; N, 8.43;  $\text{H}_2\text{O}$ , 6.00. Found: C, 49.77; H, 7.49; N, 8.24;  $\text{H}_2\text{O}$ , 6.06). The lactam did not give a color with the hydroxylamine reagent (7). The infrared spectrum showed a lactam band (8) at 1690  $\text{cm}^{-1}$ , there being no secondary amide band in accord with the cyclic nature of the amide function. In carbon tetrachloride bands at 3450, 3220 and 3130  $\text{cm}^{-1}$  due to the NH group (9) were present. The above spectral data are in agreement with the proposed structure. Hydrolysis of the isopropylidene group in aqueous sulfuric acid on the steam bath afforded crystalline 4-amino-4-deoxy-D-erythrulactam

(V), m.p. 153-4°;  $[\alpha]_D^{25} -17^\circ$  (c., 0.2 in  $\text{H}_2\text{O}$ );  $\lambda$  max 1700  $\text{cm}^{-1}$  (C=O) (Calcd. for  $\text{C}_4\text{H}_7\text{NO}_3$ : N, 11.96. Found: N, 12.01). In contrast to 5-amino-5-deoxy-D-ribonolactam (1), V showed no tendency to isomerize to the four-membered lactone during the acid treatment.

Very recently, a sugar derivative containing nitrogen in a five-membered ring was reported by Jones and Szarek (10). Selective periodate oxidation of 1-acetamido-1-deoxy-D-ribitol at  $\text{C}_4\text{-C}_5$  gave a homogeneous sirup which was characterized as 4-acetamido-4-deoxy-L-erythrofuranose (VIII) by its conversion to a sirupy methyl glycoside and by infrared and n.m.r. studies.

We have prepared VIII in low yield (18-20%) from the ammonia degradation of 5-acetamido-1,1-bis(ethylsulfonyl)-1,5-dideoxy-L-arabinitol (VII). Oxidation of 5-acetamido-5-deoxy-L-arabinose diethyl dithioacetal (11) (VI) with perpropionic acid at -10° afforded VII as a hygroscopic solid which when kept in dilute ammonium hydroxide (pH 11) for 2-3 days at room temperature produced a major reducing spot (reaction was followed by thin layer chromatography). Separation of this component by cellulose column chromatography afforded a colorless sirup having the same chromatographic properties (10) as VIII. The ammonia degradation of 1,1-bis(alkylsulfonyl) derivatives of terminal acetyl amino sugars to give the corresponding cyclic products containing nitrogen as the ring atom has been recently reported (12).

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