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β-L-IDOFURANOSE DERIVATIVES CONTAINING HETEROCYCLIC RING AT C-5 AND C-6

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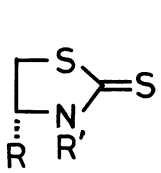
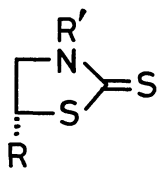
Two pairs of 3-O-benzyl-1,2-O-isopropylidene-β-L-idofuranose derivative containing thiazolidine-2-thione and oxazoline-rings at C-5 and C-6 were synthesized.

Carbohydrate derivatives having fused heterocycles at C-1 and C-2, or C-2 and C-3 have been extensively studied.[1] However, very few having a heterocycle at C-5 and C-6 have been reported. This paper communicates syntheses of L-idofuranose derivatives containing thiazolidine-2-thione or 2-oxazoline ring at C-5 and C-6 position.

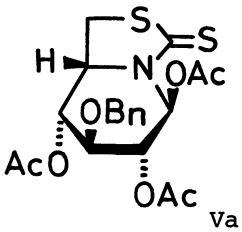
Treatment of 3-O-benzyl-5,6-dideoxy-5,6-epimino-1,2-O-isopropylidene-β-L-idofuranose (I),[2] which was prepared from 6-azido-3-O-benzyl-6-deoxy-1,2-O-isopropylidene-5-O-methanesulfonyl-α-D-glucofuranose (mp 79.5 - 80.5°C, $[\alpha]_D^{22}$ -39.0°) by an improved method, with carbon disulfide[3] in a sealed tube at 100°C for 6 hr gave the corresponding 4-[2-thioxothiazolidin-(4R)-yl]-α-D-xylo-tetrofuranose (IIa) (mp 140 - 141°C, $[\alpha]_D^{22}$ -32.1°) in 84% maximum yield at 1.2 mmol/ml concentration of I. Moreover, catalytic reduction of 6-azido-6-deoxy-1,2-O-isopropylidene-5-O-p-toluenesulfonyl-α-D-glucofuranose[2] in ethanol in the presence of palladium-charcoal and a slight excess of acetic acid, and successive refluxing of the product with 2 equimolar amount of potassium hydroxide and excess carbon disulfide[4] in ethanol for 4 hr gave another isomeric [2-thioxothiazolidin-(5R)-yl] derivative (IIIa) (mp 120 - 125°C, $[\alpha]_D^{22}$ +5.8°). Both structures were deduced from their preparations,[3,4] and confirmed by comparison of NMR spectrum of IIa with that of its N-acetate (IIb: sirup, $[\alpha]_D^{22}$ -295°). N-Acetylation of IIa caused a lower shift (1.43 ppm) of H_4 and a higher shift (0.68 ppm) of one of H_5 proton signals, depending on the acetylation shift[5] and the anisotropic effect of the acetyl group, respectively. In the case of IIIa and its acetate (IIIb: mp 150 -



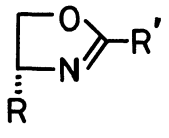
IIa: R'= H
IIb: R'= Ac



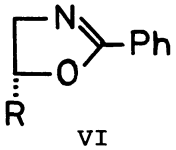
IIIa: R'= H
IIIb: R'= Ac



IV

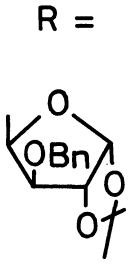


Va: R'= p-nitrophenyl
Vb: R'= p-anisyl



VI

R =



151°C, $[\alpha]_D^{22}$ +34.5°), the above shifts were not so remarkable. Hydrolysis of the isopropylidene group of IIa and successive acetylation gave a new class of bicyclic compound: (5R,6R,8S)-triacetoxy-(7R)-benzyloxy-perhydropyrido[1,2-c]-(8aR)-2-thioxothiazole (IV: mp 129 - 130°C, $[\alpha]_D^{22}$ -82.0°) in 72% yield. The structure of IV was deduced from the lack (δ 1.95, 2.02, 2.08) of the characteristic N-acetyl proton signal (Ib: δ 2.72, IIb: δ 2.68) in its NMR spectrum. Similar conversion of IIIa gave the corresponding furanose derivative (NAc: δ 2.72, OAc: δ 2.04) as a sirup.

On the other hand, treatment of I with aroyl chloride and triethylamine in dry benzene gave the corresponding N-aroyl derivatives in fairly good yields (a: p-nitrobenzoyl, mp 123 - 124°C, $[\alpha]_D^{22}$ -51.8°; b: p-anisoyl, sirup, $[\alpha]_D^{22}$ -55.3°), which were refluxed with sodium iodide in absolute acetone[6] overnight to give 3-O-benzyl-1,2-O-isopropylidene-4-[2-p-nitrophenyl-4,5-dihydro-1,3-oxazol-(4R)-yl]-(Va: mp 193 - 194°C, 96%, $[\alpha]_D^{22}$ -50.3°) and -[2-p-methoxyphenyl-4,5-dihydrooxazol-(4R)-yl]-α-D-xylo-tetrofuranose (Vb: sirup, 85%, $[\alpha]_D^{22}$ -51.0°). Moreover, treatment of 3-O-benzyl-6-benzamido-6-deoxy-1,2-O-isopropylidene-5-O-tosyl-α-D-glucofuranose with excess sodium acetate in 97% ethanol at 90°C for 24 hr[7] gave isomeric [2-phenyl-4,5-dihydro-1,3-oxazol-(5R)-yl] derivative (VI: sirup, $[\alpha]_D^{22}$ -97.6°) in 51% yield. Structures of all new compounds were supported by analytical and IR data. Optical rotations were measured in $CHCl_3$ unless otherwise stated.

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