SYNTHESIS OF L-IDOPYRANOSE DERIVATIVES HAVING A PHOSPHORUS ATOM IN THE HEMIACETAL RING

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Reaction of 3-O-acetyl-5,6-dideoxy-1,2-O-isopropylidene-6-nitro-α-D-xylo-hexo-5-enofuranose with excess phenylphosphine in anhydrous benzene at 40-50 °C followed by evaporation of the solvent and separation of the product by column chromatography on silica gel gave 3-O-acetyl-5,6-dideoxy-1,2-O-isopropylidene-6-nitro-5-C-(phenylphosphino)-β-L-idofuranose, 3-O-acetyl-5,6-dideoxy-1,2-O-isopropylidene-6-nitro-5-C-(phenylphosphino)-α-D-glucofuranose, and a 2:1 adduct in 51, 14, and 35% yield, respectively.

Hydrolysis of 3-O-acetyl-5,6-dideoxy-1,2-O-isopropylidene-6-nitro-5-C-(phenylphosphino)-β-L-idofuranose followed by treatment of the product with ozone in the presence of sodium methoxide in methanol at - 78 °C afforded 5-C-(phenylphosphinyl)-L-ido-hexodialdo-1,5-pyranose in 88% yield. Reduction of the aldehyde by sodium borohydride in methanol at room temperature overnight gave 5-C-(phenylphosphinyl)-L-idopyranose in 100% yield.

The structure of 5-C-(phenylphosphinyl)-L-idopyranose was confirmed by acetylation of the compound by acetic anhydride-pyridine to give 1,2,3,4,6-penta-O-acetyl-5-C-(phenylphosphinyl)-L-idopyranose, which was first synthesized.