A Chemical Synthesis of Panose

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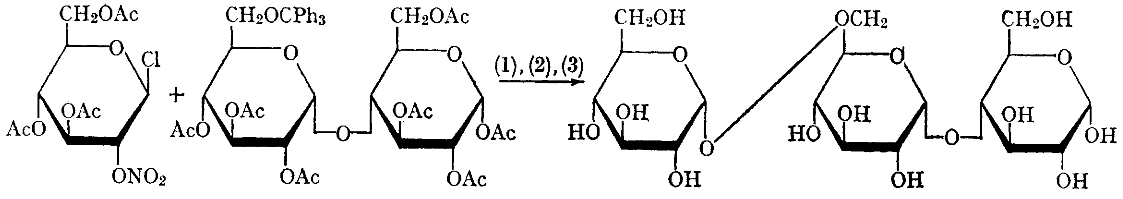
WE report a chemical synthesis of panose[1] (III) effected by the reaction between 3,4,6-tri-*O*-acetyl-2-*O*-nitro-β-D-glucopyranosyl chloride[2] (I) and 1,2,2′,3,3′,4′,6-hepta-*O*-acetyl-6′-*O*-trityl-α-maltose (II). The 2-nitrate derivative prevents undesirable neighbouring-group participation and results in the formation of an α-D-glucosidic linkage. The use of a trityl ether in this type of reaction has been reported by Bredereck and co-workers.[3] Tritylation of maltose in pyridine with 1 mole of trityl chloride, subsequent acetylation, and isolation by chromatography on a silica-gel column (benzene–ethyl acetate, 6:4 v/v, developer), led to the formation of three crystalline products: 1,2,2′,3,3′,4′-hexa-*O*-acetyl-6,6′-di-*O*-tritylmaltose (13%, m.p. 222—223° with sintering at 213°, $[\alpha]_D^{20}$ + 88°, *c*, 2·14 in chloroform) and two hepta-*O*-acetyl-*O*-tritylmaltose derivatives (A, 31% and B, 3·3%) with the constants: (A), m.p. 164—164·5°, $[\alpha]_D^{20}$ + 99° (*c*, 2·17 in chloroform); (B), m.p. 189—190°, $[\alpha]_D^{20}$ + 101° (*c*, 1·78 in chloroform). The ditrityl derivative has been reported by Josephson[4] who recorded a melting point of 116—119° and the same rotation. It is probable that we have isolated a higher melting dimorphous form of this substance. The dextrorotations of the two (6 or 6′)-*O*-trityl acetates establishes their α-D-anomeric nature. To determine the location of the trityl groups in each of these derivatives, an authentic sample of 1,2,2′,3,3′,4′,6′-hepta-*O*-acetyl-6-*O*-trityl-α-maltose was prepared by anomerization of 1,2,2′,3,3′,4′,6′-hepta-*O*-acetyl-6-*O*-trityl-β-maltose, synthesized through 1,2,2′,3,3′,4′,6′-hepta-*O*-acetyl-β-maltose,[5] by tritylation, deacetylation, and reacetylation with acetic anhydride and pyridine. Thus (B) is 1,2,2′,3,3′,4′,6′-hepta-*O*-acetyl-6-*O*-trityl-α-maltose and (A) is the isomeric (II).



(I) (II) (III)

(1) $AgClO_4$; (2) H_2–Pd; (3) NaOMe

Equimolar amounts of (I) and (II) were treated for 20 min. at room temperature and in nitromethane solution, with silver perchlorate and Drierite after which the nitrate group was removed by hydrogenation with palladium catalyst. After deacetylation and deionization with Dowex-50 (H^+), the reaction products were chromatographed on a carbon–Celite column by successive development with water, 5%, 10%, 15%, and 30% aqueous ethanol. The eluate material recovered from the combined third and fourth eluates was crystallized from warm methanol; m.p. 221° dec. unchanged on admixture with an authentic specimen of panose (first dimorphous form)[6]; *X*-ray powder diffraction date identical with those recorded[6] for this form.

All new substances showed proper elemental analyses and were homogeneous by thin-layer chromatography.

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