Synthesis of Methyl 2-O-Benzoyl-4, 6-O-benzylidene-α -D-arabino-hexopyranosid-3-ulose

Synthesis of Methyl 2-*O*-Benzoyl-4, 6-*O*-benzylidene-α-D-*arabino*-hexopyranosid-3-ulose#

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For the study of virus-inactivating action of pyranosiduloses, methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-*arabino*-hexopyranosid-3-ulose (**4**) which has an axial α-substituent in the molecule was synthesized by oxidation of methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-mannopyranoside (**1**) and methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-altropyranoside (**2**) with DMSO-acetic anhydride mixture.

Examination of the time course of the oxidation reactions by p. m. r. spectroscopy revealed that compound **4** was epimerized to thermodynamically more favourable epimer, methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose (**6**) during the reaction. Treatment of **1** with the oxidant at 35° for 2.5 hr, followed by evaporation of the solvent and reagent afforded **4** in 90% yield. The D-*arabino* structure of **4** was confirmed by the elemental analysis and the examination of p. m. r. data for **4**, **6**, and crystalline 2, 4-dinitrophenyhydrazone derivatives (**5** and **7**) of **4** and **6**.

Introduction

This laboratory has been interested in the synthesis and biological activity of hexopyranosiduloses.[1] During the course of our recent study on the virus-inactivating action of methyl hexopyranosid-3-ulose derivatives,[2] methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-*arabino*-hexopyranosid-3-ulose (**4**) and its C-2 epimer (**6**) were required. Most substituted hexopyranosid-3-uloses have recently been prepared by oxidation of appropriate substituted carbohydrate derivatives containing an isolated secdonary hydroxyl group at C-3, with recently developed new oxidants, such as dimethyl sulfoxide (DMSO) based oxidants or ruthenium oxide.[3,4] However, preparation of pyranosiduloses with an axial α-substituent has been sometimes difficult because of epimerization of the ketones during oxidation to thermodynamically favourable product, i.e. an epimer with an equatorial α-substituent,[5,6] although some cases without epimerization have also been reported.[7,8] The present paper reports the formation of **4** from methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-mannopyranoside (**1**) or methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-altropyranoside (**2**), and epimerization of **4** to methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose (**6**) during oxidation with DMSO-acetic anhydride mixture. The use of pyridinium chlorochromate for preparation of hexopyranosiduloses without epimerization was recently reported.[9]

Results and discussion

Methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-*arabino*-hexopyranosid-3-ulose (**4**) can be prepared by oxidation of C-3 hydroxyl group of methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-mannopyranoside (**1**) or methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-altropyranoside (**2**) unless epimerization of C-3 substituent to *ribo* derivative takes place. Compound **1** was prepared by selective benzoylation of methyl 4, 6-*O*-benzylidene-α-D-mannopyranoside[10] with benzoyl cyanide[11], followed by separation of the reaction products by silica gel column chromatography in 18% yield. Other products separated were methyl

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2, 3-di-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-mannopyranoside (18%), and methyl 3-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-mannopyranoside (4%), respectively. Syrupy **1** was converted into cyrstalline methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-3-*O*-*p*-tolylsulfonyl-α-D-mannopyranoside (**8**). The structure of **8** was confirmed by examination of p. m. r. data for **8** and **1** (chemical shift and coupling constants of C-2 protons, see experimental section). Similarly, compound **2** was prepared by selective benzoylation of methyl 4, 6-*O*-benzylidene-α-D-altropyranoside.[12] In this case, compound **2** was obtained as main product in 70% yield.

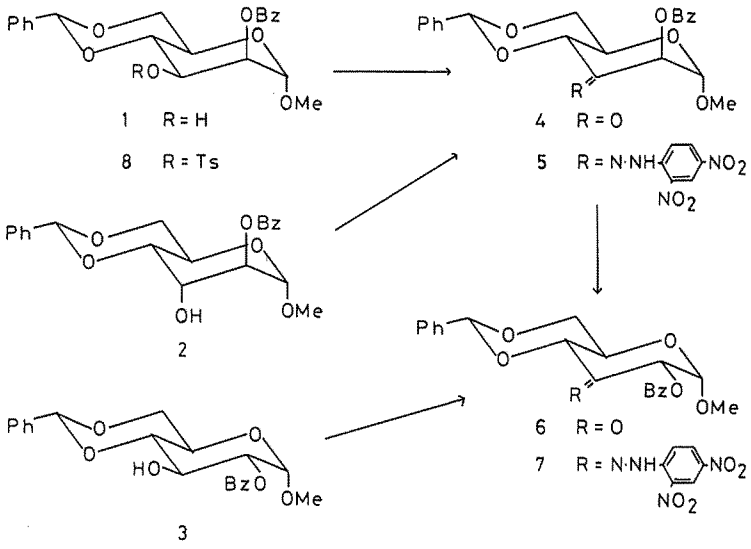

Fig. 1.

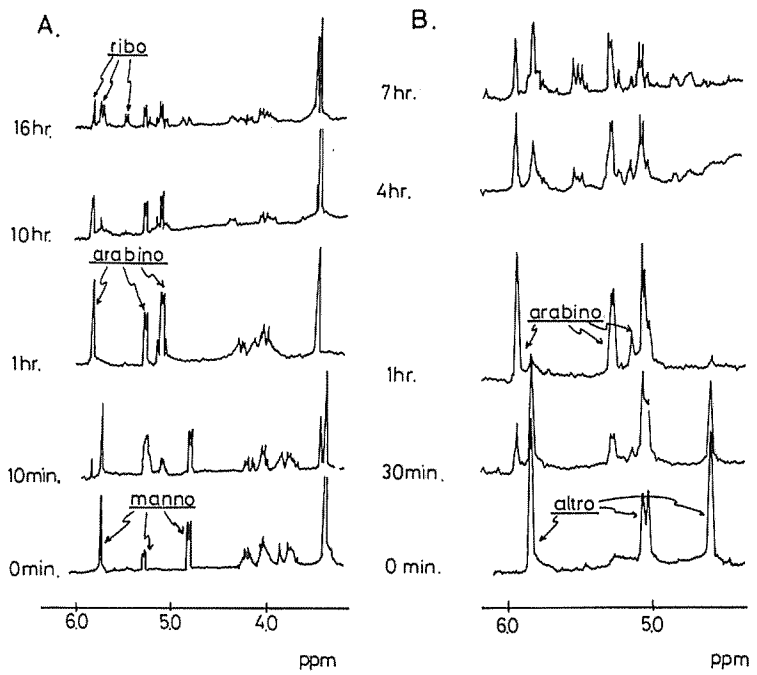

Fig. 2. P. m. r. spectra of the reaction mixtures for the preparation of **4** from **1** (A) and **2** (B).

For optimal reaction conditions for the preparation of **4**, the reaction of **1** with DMSO-acetic anhydride mixture at 35° was monitored by p. m. r. spectroscopy. Figure 2–A shows the spectra of the reaction mixture which contained 25 mg of **1**, 0.25 ml of acetic anhydride, and 0.4 ml of DMSO-D_6. After 1 hour of reaction time, signals of H-1, H-2, and benzylidene methine proton of **1** completely disappeared, and the same kind of signals of compound **4** appeared. After 16 hours, the reaction mixture contained additional product whose signals corresponded well with those of methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-ulose (**6**) which was prepared by oxidation of methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-D-glucopyranoside (**3**). Figure 2–B shows the similar results obtained by treatment of **2** with DMSO-D_6-acetic anhydride mixture at 35°. These results reveal that oxidation of **1** and **2** ends in 1 hour, whereas epimerization of **4** to **6** starts after oxidation, suggesting that reaction intermediates of oxidation, such as sulphonium "ylid", may not be involved in epimerization. These results were in agreement with earlier observation that an epimeric pair of isolated hydroxyl group of carbohydrates were oxidized at an equal rate[13] and that pyranosiduloses containing an axial α-substituent were epimerized to thermodynamically stable isomer. A. C. Richardson *et al.* suggested acid-catalyzed enolization as possible mechanism for the observed epimerization of sugar ketones.[6]

Preparation of **4** on larger scale was accomplished by treating **1** (100 mg), acetic anhydride (1.0 mg), and DMSO (1.6 ml) at 35° for 2.5 hr to afford chromatographically (t. l. c.) homogenous syrupy product in 90% yield. The structure of **4** was further confirmed by converting **4** into crystalline 2, 4-dinitrophenylhydrazone derivative (**5**). P. m. r. data for **5** ($J_{1,2}$=0.3 Hz, vicinal diequatorial protons), elemental analysis, and comparison of properties of **5** with those of methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-α-*ribo*-hexopyranosid-3-ulose 2, 4-dinitrophenylhydrazone (**7**, $J_{1,2}$=4.5 Hz, vicinal equatorial-axial protons) completely support the *arabino* structure for **4** and **5**.

In conclusion, the present study has shown that hexopyranosiduloses with an axial α-substituent can easily be prepared in good yield by oxidation with DMSO based oxidants of the corresponding alcohols if the reaction is stopped before epimerization of desirable product to thermodynammically favourable epimer takes place. It may be of interest to note that oxidation of **1** or **2** with DMSO-acetic anhydride come to an end in about 1 hour which is quite shorter than the reaction time hitherto reported for the oxidation of secondary hydroxyl groups of carbohydrates.[14]

Experimental

General methods. Melting points were determined on a Yanagimoto micro hot stage and are uncorrected. Infrared spectra were measured with a Jasco infrared spectrophotometer (IR-G). Optical rotations were determined in 0.1 dm cells with a Jasco optical dispersion recorder. Thin-layer chromatography was carried out on Merck (Darmstadt) plates precoated with silica gel F-254, and spots were located with a Shimazu high speed TLC scanner CS-920. Solvent system used was benzene: ethyl acetate=6: 1 v/v. Evaporations were carried out *in vacuo* at 40–45°. P.m.r. spectra were recorded with a Hitachi high resolution spectrometer R-22.

Methyl 2-O-*benzoyl*-4, 6-O-*benzylidene*-α-D-arabino-*hexopyranosid*-3-*ulose* (**4**) A mixture of **1** (100 mg) and acetic anhydride (1.0 *ml*) in DMSO (1.6 *ml*) was stirred at 35° for 2.5 hr. Evaporation of the reaction mixture *in vacuo*, followed by extraction of the resulting syrup with three portions of chloroform (30 ml) and concentration of the chloroform solution, afforded syrupy ulose (90 mg, 90%), R_f 0.12, ν_{max}^{film} 1730, 1759 cm^{-1}; p.m.r. ($CDCl_3$)δ3.45 (s, 3 H, OMe), 3.80–4.50 (multiplet, 3 H, H-5, 6, and 6′), 4.80 (q, 1 H, H-4), 5.15 (d, 1 H, H-2, $J_{2,1}$=3.0 Hz), 5.28 (d, 1 H, H-1, $J_{1,2}$=3.0 Hz), 5.60 (s, phC*H*, 1 H), 7.30–7.60 (multiplet, aromatic), 8.05 (q, aromatic); (DMSO-D_6)δ4.92 (d, 1 H, H-2, $J_{2,1}$=1.5 Hz), 5.09 (d, 1 H, H-1), 5.87 (s, 1 H, phC*H*).

Methyl 2-O-*benzoyl*-4, 6-O-*benzylidene*-α-D-*arabino*-*hexopyranosid*-3-*ulose* 2, 4-*dinitrophenylhydrazone* (**5**). To a solution of **4** (100 mg) in methanol was added 1.0 ml of 2, 4-dinitrophenylhydrazine reagent[15] at room temperature to afford crude crystalline hydrazone. Purification of the crude product by preparative t.l.c. (0.5 mm) gave pure, yellow crystalline hydrazone (35 mg), m.p. 178–180°, $[\alpha]_D^{13}=-475°$ (*c*, 0.2, chloroform), R_f 0.62, ν_{max}^{KBr} 3250, 1720, 1510, 1342 cm^{-1}; p.m.r. ($CDCl_3$)δ3.45 (s, 1 H, OMe), 4.67 (d, 1 H, H-4, $J_{4,5}$=9.0 Hz), 5.12 (d, 1 H, H-2, $J_{2,1}$= 0.3 Hz), 5.70 (s, 1 H, phC*H*), 5.85 (d, 1 H, H-1, $J_{1,2}$=0.3 Hz), 8.12 (d, aromatic), 8.33 (q, aromatic), 8.84 (d,

aromatic).

Anal. Calc. for $C_{27}H_{24}O_{10}N_4$: C, 57.44; H, 4.28; N, 9.93. Found: C, 57.39; H, 5.38; N, 9.84.

Methyl 2-O-*benzoyl*-4, 6-O-*benzylidene*-α-D-*manopyranoside* (**1**) To a solution of methyl 4, 6-*O*-benzylidene-α-D-mannopyranoside[10] (8 g) in acetonitrile (10 ml) was added benzoyl cyanide (3.73 g) and the reaction mixture was kept at room temperature for 30 min with stirring. After methanol (5 ml) was added to the reaction mixture, the solution was concentrated to the syrupy residue which was found by t.l.c. to contain four products. Separation of the products on silica gel column chromatography (eluent, benzene: ethylacetate=1: 6) afforded the title compound (2.3 g, 18% yield), together with 3-*O*-benzoyl derivative (0.6 g, 4% yield) and 2, 3-di-*O*-benzoyl derivative (2.3 g, 18% yield); *methyl* 2-O-*benzoyl*-4, 6-O-*benzylidene*-α-D-*mannopyranoside*, syrup, R_f 0.45, ν_{max}^{film} 3500, 1725 cm^{-1}, p.m.r. ($CDCl_3$)δ 3.40 (s, 3 H, OMe), 3.80–4.40 (multiplet, 4 H, H-3, 4, 6, 6′), 4.83 (d, 1 H, H-1, $J_{1,2}$=0.8 Hz), 5.45 (q, 1 H, H-2, $J_{2,4}$=4.0 Hz), 5.65 (s, 1 H, phC*H*), 7.30–7.60 (multiplet, aromatic), 8.10 (q, 2 H, aromatic); (DMSO-D_6)δ4.81 (d, 1 H, H-1, $J_{1,2}$=1.5 Hz), 5.23 (t, 1 H, H-2), 5.76 (s, 1 H, phC*H*).; *methyl* 3-O-*benzoyl*-4, 6-O-*benzylidene*-α-D-*mannopyranoside*, m.p. 127° (lit.[11] m.p. 132°), R_f 0.22, ν_{max}^{KBr} 3500, 1725 cm^{-1}, p.m.r. ($CDCl_3$)δ3.42 (s, OMe), 3.80–4.40 (multiplet, 5 H, H-2, 4, 5, 6, 6′), 4.80 (d, 1 H, H-1, $J_{1,2}$=0.8 Hz), 5.67 (s, 1 H, phC*H*), 5.58 (q, 1 H, H-3, $J_{3,2}$=3.0 Hz, $J_{3,4}$=10.0 Hz), 7.30–7.60 (multiplet, aromatic), 8.09 (q, 2 H, aromatic); *methyl* 2, 3-*di*-O-*benzoyl*-4, 6-O-*benzylidene*-α-D-*mannopyranoside*, syrup, R_f 0.70, ν_{max}^{film} 1730 cm^{-1}, p.m.r. ($CDCl_3$)δ3.46 (s, 3 H, OMe), 3.70–4.50 (multiplet, 4 H, H-4, 5, 6, 6′), 4.91 (s, 1 H, H-1, $J_{1,2}$=0.8 Hz), 5.68 (s, 1 H, phC*H*), 5.71 (q, 1 H, H-2, $J_{2,3}$=3.0 Hz), 5.89 (q, 1 H, H-3, $J_{3,4}$=8.0 Hz), 7.20–7.60 (multiplet, aromatic), 8.00 (q, aromatic 2 H).

Methyl 2-O-*benzoyl*-4, 6-O-*benzylidene*-3-O-p-*tolylsulfonyl*-α-D-*mannopyranoside* (**8**) Treatment of **4** (50 mg) with *p*-tolylsulfonyl chloride (100 mg) in pyridine (3.5 ml) at room temperature for 4 days followed by the usual work up of the reaction mixture afforded the title compound in 40.3% yield, m.p. 183–185° (lit.[11] m.p. 186–188°), $[\alpha]_D^{13}$+500° (*c*, 0.014, chloroform), R_f 0.66, ν_{max}^{KBr} 1732, 1778, 1180 cm^{-1}, p.m.r. ($CDCl_3$)δ2.28 (s, 3 H, phCH_3), 3.39 (s, 3 H, OMe), 3.70–4.30 (multiplet, 4 H, H-4, 5, 6, 6′), 4.74 (d, 1 H, H-1, $J_{1,2}$=1.6 Hz), 5.05 (q, 1 H, H-3, $J_{3,4}$=10.0 Hz), 5.50 (q, 1 H, H-2, $J_{2,3}$=4.0 Hz), 5.54 (s, phC*H*, 1 H), 6.90–8.20 (multiplet, aromatic).

Methyl 2-O-*benzoyl*-4, 6-O-*benzylidene*-α-D-*ribo-hexopyranosid*-3-*ulose* (**6**) Oxidation of **3** with DMSO-acetic anhydride by the method of F. A. Carey[16], gave the title compound in 39% yield, m.p. 197–204° (lit.[16] m.p. 210–212°), $[\alpha]_D^{13}$=+68.0 (*c*, 0.88, chloroform, R_f 0.53, ν_{max}^{KBr} 1700, 1762 cm^{-1}, p.m.r. ($CDCl_3$)δ3.49 (s, 3 H, OMe), 3.80–4.50 (multiplet, 4 H, H-4, 5, 6, 6′), 5.36 (d, 1 H, H-2, $J_{2,1}$=4.2 Hz), 5.65 (d, 1 H, H-1), 5.61 (s, phC*H*, 1 H), 7.30–7.60 (multiplet, aromatic), 8.15 (q, 2 H, aromatic); (DMSO-D_6)δ4.92 (d, 1 H, H-4, $J_{4,5}$=10.0 Hz), 5.50 (d, 1 H, H-2, $J_{2,1}$=4.5 Hz), 5.76 (d, 1 H, H-1, $J_{1,2}$=4.5 Hz), 5.77 (s, 1 H, phC*H*).

Methyl 2-O-*benzoyl*-4, 6-O-*benzylidene*-α-D-*ribo-hexopyranosid*-3-*ulose* 2, 4-*dinitrophenylhydrazone* (**7**) To a solution of **6** (50 mg) in methanol was added the 2, 4-dinitrophenylhydrazine reagent (0.5 ml) to give crude hydrazone. Recrystalization from ethanol afforded yellow needles (49 mg, 67%), m.p. 300°, $[\alpha]_D^{13}$=+57° (*c*, 0.7, chloroform), R_f 0.52, ν_{max}^{KBr} 3250, 1732, 1520, 1340 cm^{-1}; p.m.r. ($CDCl_3$)δ2.98 (s, 3 H, OMe), 3.20–3.90 (multiplet, H-5, 6, 6′), 4.11 (d, 1 H, H-4, $J_{4,5}$=9.0 Hz), 4.53 (d, 1 H, H-2, $J_{2,1}$=4.0 Hz), 5.02 (s, 1 H, phC*H*), 5.08 (d, 1 H, H-1, $J_{1,2}$=4.0 Hz), 6.70–7.05 (multiplet, aromatic), 7.15 (q, 2 H, aromatic), 7.55 (q, 1 H, aromatic), 8.24 (d, 1 H, aromatic), 8.90 (d, 1 H, aromatic).

Anal. Calc. for $C_{27}H_{24}O_{10}N_4$: C, 57.44; H, 4.28; N, 9.93. Found: C, 57.28; H, 4.25; N, 9.78.

Methyl 2-O-*benzoyl*-4, 6-O-*benzylidene*-α-D-altropyranoside (**2**) Benzoylation of methy 4, 6-*O*-benzylidene-α-D-altropyranoside (1.0 g) with benzoyl cyanide (0.52 g) in acetonitrile (5 ml) at 25° for 15 min, followed by the usual work up of the reaction mixture gave syrupy product which was chromatographed on silica gel to yield the title compound as main product (433 mg), m.p. 136–137° (lit.[11] m.p. 137–138.5°), p.m.r. ($CDCl_3$)δ3.48 (s, 3 H, OMe), 3.80–4.10 (mlutiplet, 2 H, H-6, 6′), 4.2–4.4 (multiplet, 3 H, H-3, H-4, H-5), 4.83 (s, 1 H, H-1), 5.30 (q, 1 H, H-2, $J_{2,1}$=0.5 Hz, $J_{2,3}$=1.5 Hz), 5.71 (s, 1 H, phC*H*), 7.3–7.6 (multiplet, aromatic), 8.05–8.15 (q, 2 H, aromatic); (DMSO-D_6)δ3.33 (s, 3 H, OMe), 3.7–4.5 (multiplet, 5 H, H-3, 4, 5, 6, 6′), 4.70 (s, 1 H, H-1), 5.08 (d, 1 H, H-2, $J_{2,3}$=2.6 Hz), 5.33 (d, 1 H, C_3-O*H*), 5.80 (s, 1 H, phC*H*), 7.3–7.8 (multiplet, aromatic), 8.0–8.2 (q, 2 H, aromatic).

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摘　　要

メチル 2-*O*-ベンゾイル-4,6-*O*-ベンジリデン-α-D-アラビノ-ヘキソピラノシド-3-ウロースの合成

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ヘウソピラノシドウロースの抗ウイルス活性研究に必要なα位にアキシャル置換基を有するメチル 2-*O*-ベンゾイル-4,6-*O*-ベンジリデン-α-D-アラビノ-ヘキソピラノシド-3-ウロース (**4**) を，相当する D-マンノース (**1**) および D-アルトロース (**2**) 誘導体の酸化によって合成した。**1** 又は **2** と DMSO-無水酢酸の反応を，p. m. r. によって経時的に調べたところ，**4** は生成後，C-2 エピマーのメチル 2-*O*-ベンゾイル-4,6-*O*-ベンジリデン-α-D-リボ-ヘキソピラノシド-3-ウロース (**6**) に異性化することがわかったので，反応を異性化の起る前にとめて，目的物を90%の収量で離することができた。**4** は結晶性の2,4-ジニトロフェニルヒドラゾン (**5**) に導き，**6** のヒドラゾンとの比較，p. m. r. および元素分析により，その構造が D-アラビノ型であることを確認した。