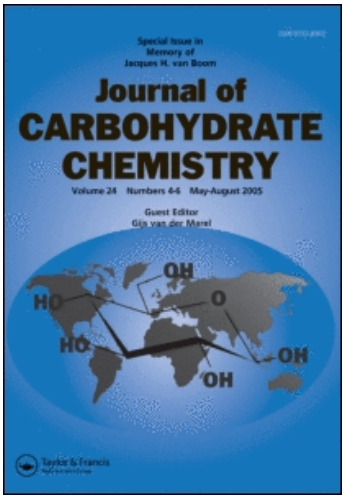

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Synthetic Application of Partially Protected Fructopyranoses

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SYNTHETIC APPLICATION OF PARTIALLY PROTECTED FRUCTOPYRANOSES

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ABSTRACT

Partial deacetonation of 1-O-benzoyl-2,3:4,5-di-O-isopropylidene-β-D-fructopyranose (2) yielded the related 2,3-O-isopropylidene derivative (3) that was subsequently transformed into the corresponding 1-O-benzoyl-4,5-O-dibutylstannylene-2,3-O-isopropylidene-β-D-fructopyranose (4). Reaction of 4 with benzyl bromide proceeded with high regioselectivity to afford 1-O-benzoyl-5-O-benzyl-2,3-O-isopropylidene-β-D-fructopyranose (5) together with a small quantity of the 4-O-benzyl derivative (6). Oxidation of 5 gave the 4-oxo derivative (10) which was reduced to yield a mixture of 5 and its 4-epimer (11). Debenzylation of 11, followed by a debenzoylation reaction produced 2,3-O-isopropylidene-β-D-tagatopyranose (13). Acetonation of 13 yielded 1,2:3,4-di-O-isopropylidene-α-D-tagatofuranose (14). Structures and configurations of the above compounds were established on the basis of their analytical and spectroscopic data.

INTRODUCTION

Partial protection of the funtional groups present in sugars is an excellent tool for making structural or configurational changes in a specific chiral centre of such compounds. Thus, the partial protection of fu-

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ranose as well as pyranose derivatives of sugars through the regioselective ring opening of the corresponding O-stannylene derivatives has been reported[1].

On the other hand, we are interested in the synthesis of D-tagatose from the more common D-fructose derivatives by changing the configuration at C-4 of the latter compounds. This could be easily achieved by oxidation of the corresponding secondary alcohol to a carbonyl group followed by stereoselctive or stereospecific reduction[2]. Thus, the synthesis of a D-tagatofuranose derivative from 1,6-di-O-benzoyl-2,3-O-isopropylidene-β-D-fructofuranose by the above method has been reported[3].

In the present paper we communicate the results found in the use of an O-stannylene derivative of D-fructopyranose in the synthesis of D-tagatopyranose derivatives.

RESULTS AND DISCUSSION

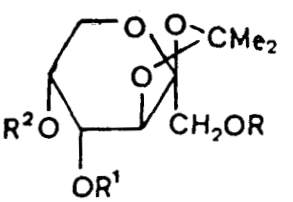
Partial hydrolysis of 1-O-benzoyl-2,3:4,5-di-O-isopropylidene-β-D-fructopyranose (2) gave the corresponding 2,3-O-isopropylidene derivative (3). Reaction of compound (3) with dibutyltin oxide gave a product (not isolated) whose ^{1}H NMR spectrum corresponded to 1-O-benzoyl-4,5-O-dibutylstannylene-2,3-O-isopropylidene-β-D-fructopyranose (4). The subsequent reaction of 4 with benzyl bromide afforded two products identified (see below) as 1-O-benzoyl-5-O-benzyl-2,3-O-isopropylidene-β-D-fructopyranose (5, 97%) and its 4-O-benzyl analogue 6 (2.8%). The structures of 5 and 6 were established through their 1,4- (7) and 1,5-di-O-benzoyl derivatives (8), respectively. Thus, in the ^{1}H NMR spectrum of 7, H-4 appeared as a triplet signal (δ 5.97), $J_{3,4} \simeq J_{4,5}$), whereas H-5 in 8 appeared as a septet (δ 5.47)

according to the presence of three vicinal hydrogen atoms.

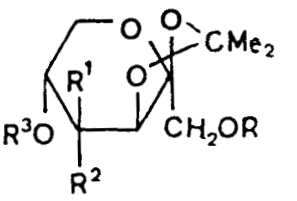
The high regioselectivity found in the ring opening of the O-dibutylstannylene derivative (4) by benzyl bromide is in agreement with that previously reported[1b], only if we consider that the most stable conformation for 4 is that shown by A ($^6S_4$). According to the data found in the literature[4], it is stated that a pyranose cis-fused to a 1,3-dioxolane ring must adopt such a skew-boat conformation. The change of an O-isopropylidene by an O-dibutylstannylene group must have little conformational significance, since the ^{1}H NMR spectrum of 4 showed a value of $J_{3,4}$ = 4 Hz, which is not consistent with a trans-diaxial disposition of H-3,4 in a $^1C_4$ conformation (B). As can be seen, the oxygen atom at C-5 in A adopts a quasi-equatorial position, and hence the attack of the benzyl bromide occurred at that position[1b] to yield preferentially compound (5).

Oxidation of 5 to 10 was carried out with ruthenium tetraoxide[5] and trifluoroacetic anhydride-methyl sulfoxide[6], the latter being the better procedure. On the other hand, the low stereoselectivity found in the reduction of 10 to 11 could be due to the fact that in the most stable conformation for 10, perhaps as a consequence of the effects mentioned above, the carbonyl group adopts a disposition in which the probability of an equatorial or axial attack is about the same.

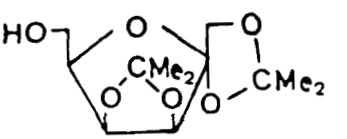
Finally, the structure of 11, as well as those of 12 and 13, were definitively demonstrated by the transformation of the latter into the well known 1,2:3,4-di-O-isopropylidene-α-D-tagatofuranose (14)[7].



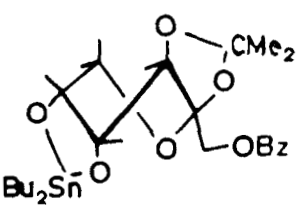
1 R=H; $R^1=R^2=CMe_2$
2 R=Bz; $R^1=R^2=CMe_2$
3 R=Bz; $R^1=R^2=H$
4 R=Bz; $R^1=R^2=SnBu_2$
5 R=Bz; $R^1=H$; $R^2=Bn$
6 R=Bz; $R^1=Bn$; $R^2=H$
7 $R=R^1=Bz$; $R^2=Bn$
8 $R=R^2=Bz$; $R^1=Bn$
9 $R=R^1=H$; $R^2=Bn$



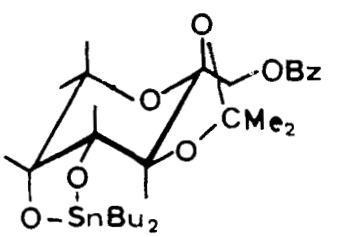
10 R=Bz; $R^1=R^2=O$; $R^3=Bn$
11 R=Bz; $R^1=OH$; $R^2=H$; $R^3=Bn$
12 R=Bz; $R^1=OH$; $R^2=R^3=H$
13 $R^1=OH$; $R=R^2=R^3=H$



14



A



B

EXPERIMENTAL

General methods. Melting points were determined with an Electrothermal melting points apparatus and are uncorrected. Solutions were dried over $MgSO_4$ before concentration under diminished pressure. ^1H NMR spectra

(200 and 80 MHz, $CDCl_3$, internal Me_4Si) were recorded with a Bruker WP-200 SY and WP-80 CW spectrometers, IR spectra with a Perkin-Elmer 782 instrument. Optical rotations were measured, unless otherwise stated, for solutions in chloroform (1 dm tube) with a Perkin-Elmer 141 polarimeter. R_f values are reported for TLC performed on Silica Gel G (Merck) with ether-hexane (3:1) and detection by charring with sulfuric acid. Column chromatography was performed on silica gel (Merck, 7734).

1-O-Benzoyl-2,3:4,5-di-O-isopropylidene-β-D-fructopyranose (2). To an ice-cold and stirred solution of 2,3:4,5-di-O-isopropylidene-β-D-fructopyranose[8] (1, 15 g, 57 mmol) in dry pyridine (70 mL) was slowly added benzoyl chloride (9 mL) and the mixture was left at room temperature overnight. Work-up of the mixture as usual then gave a residue that was subjected to column chromatography (ether-hexane, 1:2) to afford 2 (17 g, 81%), mp 78-79° (from hexane), (lit.[9] mp 81°); IR (KBr) 3068 (C-H, aromatic), 2993, 2951, and 2934 (C-H), 1729 (benzoate C=O), 1604 and 1587 (benzoate C=C), 1384 and 1378 (CMe_2), 1275 (benzoate C-O), 1251, 1164, 1124, and 1058 (1,3-dioxolane ring and C-O-C), 758 and 715 cm^{-1} (aromatic); ^1H NMR δ 8.10-8.00 and 7.60-7.30 (2 m, 5, relative intensity 2:3, Bz), 4.70 (d, 1, H-1, $J_{1,1'}$ = 11.8 Hz), 4.65 (dd, 1, H-4, $J_{3,4}$ = 2.6, $J_{4,5}$ = 8 Hz), 4.48 (d, 1, H-3), 4.32 (d, 1, H-1'), 4.28 (m, 1, H-5), 3.97 (dd, 1, H-6, $J_{5,6}$ = 1.8, $J_{6,6'}$ = 13 Hz), 3.80 (d, 1, H-6'), 1.55, 1.47, 1.37, and 1.34 (4 s, 12, 2 CMe_2).

1-O-Benzoyl-2,3-O-isopropylidene-β-D-fructopyranose (3). To a solution of 2 (17 g, 47 mmol) in methanol (100 mL) was added 1N aqueous hydrochloric acid (25 mL). The mixture was heated under reflux for 2 h, and then left at room temperature overnight. TLC then showed the presence of 1 (R_f 0.60) and 2 (R_f 0.80) together with

a new product (R_f 0.27). Neutralisation with anhydrous potassium carbonate and concentration of the solvent gave a semicrystalline residue that was extracted with ethyl acetate, evaporated and chromatographed (ether--hexane, 3:1) to afford in elution order 2 (3.3 g), 1 (225 mg), and 3 (3.55 g), which had mp 108-109° (from ether-hexane, 3:1), $[\alpha]_D$ +18° (c, 1.45); IR (KBr) 3561 and 3481 (OH), 3010 (C-H, aromatic), 2990, 2960, 2920, 2910, and 1895 (C-H), 1706 (benzoate C=O), 1604 and 1585 (benzoate C=C), 1398, 1387, and 1374 (CMe_2), 1282 (benzoate C-O), 1235, 1109, 1053, and 869 (1,3-dioxolane ring and C-O-C), 760 and 718 cm^{-1} (aromatic); ^1H NMR δ 8.10-8.00 and 7.63-7.40 (2 m, 5, relative intensity 2:3, Bz), 4.60 (d, 1, H-1, $J_{1,1'}$ = 11.8 Hz), 4.53 (d, 1, H-1'), 4.32 (d, 1, H-3, $J_{3,4}$ = 3.2 Hz), 4.29 (ddd, 1, H-4, $J_{4,5}$ = 6.7, $J_{HO,4}$ = 3.5 Hz), 4.08 (m, 1, H-5), 3.89 (dd, 1, H-6, $J_{5,6}$ = 4.8, $J_{6,6'}$ = 12 Hz), 3.78 (dd, 1, H-6', $J_{5,6'}$ = 7.6 Hz), 3.00 (d, 1, HO-4), 2.78 (d, 1, HO-5, $J_{HO,5}$ = 7.5 Hz), 1.55 and 1.39 (2 s, 6, CMe_2).

Anal. Calc. for $C_{16}H_{20}O_7$: C, 59.25; H, 6.21. Found: C, 58.47; H, 6.34.

1-O-Benzoyl-5-O-benzyl- (5) and 1-O-benzoyl-4-O--benzyl-2,3-O-isopropylidene-β-D-fructopyranose (6) via stannylene derivative (4). To a solution of 3 (2.25 g, 7 mmol) in anhydrous methanol (150 mL) was added dibutyltin oxide (1.8 g, 7.2 mmol), and the suspension was heated under reflux for 2 1/2 h to give a clear solution. Then the solvent was removed to afford syrupy 1--O-benzoyl-4,5-O-dibutylstannylene-2,3-O-isopropylidene-β-D-fructopyranose (4), that was dried under vacuum over phosphorus pentoxide overnight. ^1H NMR δ 8.20-8.00 and 7.70-7.30 (2 m, 5, relative intensity 2:3, Bz), 5.12 (d, 1, H-1, $J_{1,1'}$ = 12 Hz), 4.93 (d, 1, H-3, $J_{3,4}$ = 4 Hz), 4.83 (d, 1, H-1'), 4.73 (dd, 1, H-4, $J_{4,5}$ = 3 Hz),

4.62-4.22 (m, 2, H-5,6), 4.00 (dd, 1, H-6', $J_{5,6}$ = 6, $J_{6,6'}$ = 13.5 Hz), 1.55 and 1.40 (2 s, 6, CMe_2), 1.90--1.10 and 1.10-0.80 (2 m, 18, 2 n-Bu).

Compound (4) was taken up in dry N,N-dimethylformamide (17 mL), treated with benzyl bromide (2.5 mL, 21.4 mmol) and heated for 1 1/2 h at 100°. TLC then showed two spots (R_f 0.78 and 7.55), the main product being that of higher mobility. Evaporation of the solvent gave a residue that was dissolved in chloroform (75 mL), washed with saturated aqueous sodium chloride, water, and concentrated to give a syrup that was subjected to column chromatography (ether-hexane, 1:1) to afford syrupy 5 (2.8 g, 97%), $[\alpha]_D$ +1° (c, 1.2); IR (film) 3500 (OH), 3100, 3070, and 3040 (C-H, aromatic), 2980, 2940, and 2900 (C-H), 1725 (benzoate C=O), 1605 and 1585 (benzoate C=C), 1455 (benzyl), 1385 and 1375 (CMe_2), 1275 (benzoate C-O), 1210, 1106, and 1070 (1,3-dioxolane ring and C-O-C), 710 and 695 cm^{-1} (aromatic); ^1H NMR δ 8.11-8.02 and 7.63-7.30 (2 m, 5, relative intensity 2:3, Bz), 7.37 (s, 5, $CH_2\underline{Ph}$), 4.68 (d, 1, H-1, $J_{1,1'}$ = 12 Hz), 4.63 (s, 2, $\underline{CH_2}Ph$), 4.48 (d, 1, H-1'), 4.43-4.40 (m, 1, H-4), 4.39 (d, 1, H-3, $J_{3,4}$ = 3 Hz), 3.91 (dd, 1, H-6, $J_{5,6}$ = 2, $J_{6,6'}$ = 11 Hz), 3.91-3.88 (m, 1, H-5), 3.86 (dd, 1, H-6', $J_{5,6'}$ = 2 Hz), 2.60 (broad s, 1, HO-4), 1.55 and 1.44 (2 s, 6, CMe_2).

The second product isolated from the chromatography was syrupy 6 (80 mg, 2.8%), $[\alpha]_D$ +6° (c, 1); IR (film) 3500 (OH), 3060 and 3040 (C-H, aromatic), 2990 and 2940 (C-H), 1730 (benzoate C=O), 1605 and 1585 (benzoate C=C), 1450 (benzyl), 1380 and 1375 (CMe_2), 1275 (benzoate C-O), 1210, 1100, 1070, and 870 (1,3-dioxolane ring and C-O-C), 710 and 695 cm^{-1} (aromatic); ^1H NMR δ 8.15-7.90 and 7.65-7.20 (2 m, 5, relative intensity 2:3, Bz), 7.25 (s, 5, $CH_2\underline{Ph}$), 4.81-3.50 (m, 9,

H-1,1´,3,4,5,6,6´ and $\underline{CH_2}Ph$), 2.46 (broad s, 1, HO-5), 1.54 and 1.39 (2 s, 6, CMe_2).

1,4-Di-O-benzoyl-5-O-benzyl-2,3-O-isopropylidene--β-D-fructopyranose (7). Compound 5 (4.1 g, 10 mmol), was benzoylated in dry pyridine (40 mL) with benzoyl chloride (1.54 g, 11 mmol) in the usual manner to yield, after column chromatography (ether-hexane, 1:3) crystalline 7 (4.26 g, 82%), mp 102-103°, $[\alpha]_D$ +8° (c, 1.5); IR (KBr) 3060, 3025, and 3005 (C-H, aromatic), 2995 and 2905 (C-H), 1745 and 1730 (benzoate C=O), 1605 and 1585 (benzoate C=C), 1452 (benzyl), 1390 and 1370 (CMe_2), 1278 and 1275 (benzoate C-O), 1205, 1105, 1070, and 870 (1,3-dioxolane ring and C-O-C), 725 and 710 cm^{-1} (aromatic); ^1H NMR δ 8.05-7.90 and 7.60-7.30 (2 m, 10 relative intensity 2:3, 2 Bz), 7.27 (s, 5, $CH_2\underline{Ph}$), 5.97 (t, 1, H-4, $J_{3,4} = J_{4,5} = 3.4$ Hz), 4.71 (d, 1, H-1, $J_{1,1'} =$ 12 Hz), 4.70 (d, 1, $J_{gem,CH_2Ph} = 12$ Hz, $\underline{CH_2}Ph$), 4.59 (d, 1, $\underline{CH_2}Ph$), 4.53 (d, 1, H-1´), 4.12 (sex, 1, H-5, $J_{5,6} =$ 6.6 Hz), 3.98 (d, 2, 2 H-6), 1.69 and 1.42 (2 s, 6, CMe_2).

Anal. Calc. for $C_{30}H_{30}O_8$: C, 69.48; H, 5.83. Found: C, 69.92; H, 5.81.

1,5-Di-O-benzoyl-4-O-benzyl-2,3-O-isopropylidene--β-D-fructopyranose (8). Compound 6 (115 mg, 0.3 mmol) was benzoylated in dry pyridine (2 mL) with benzoyl chloride (0.18 g, 1.28 mmol) in the usual manner to yield, after column chromatography (ether-hexane, 1:3), syrupy 8 (140 mg, 90%), $[\alpha]_D$ -30° (c, 0.7); IR (film) 3092, 3067, and 3036 (C-H, aroamtic), 2989 and 2937 (C-H), 1726 (benzoate C=O), 1604 and 1587 (benzoate C=C), 1453 (benzyl), 1375 (CMe_2), 1269 (benzoate C-O), 1209, 1110, 1099, 1071, and 870 (1,3-dioxolane ring and C-O--C), and 711 cm^{-1} (aromatic); ^1H NMR δ 8.10-8.00, 7.65--7.40, and 7.30-7.10 (3 m, 15, 2 Bz and $CH_2\underline{Ph}$), 5.47 (sept, 1, H-5, $J_{4,5} = 3.5$, $J_{5,6} = 8$, $J_{5,6'} = 6$ Hz),

4.75 (d, 1, H-1, $J_{1,1'}$ = 12 Hz), 4.68 and 4.60 (2 d, 2, $\underline{CH_2}Ph$, J_{gem} = 12 Hz), 4.65 (d, 1, H-1'), 4.41 (d, 1, H-3, $J_{3,4}$ = 3.5 Hz), 4.34 (t, 1, H-4), 4.14 (dd, 1, H-6, $J_{6,6'}$ = 11 Hz), 4.04 (dd, 1, H-6'), 1.60 and 1.43 (2 s, 6, CMe_2).

5-O-Benzyl-2,3-O-isopropylidene-β-D-fructopyranose (9). To a solution of 7 (2.45 g, 4.7 mmol), in anhydrous methanol (70 mL), 1N sodium methoxide (2 mL) was added, and the mixture left at room temperature for 1 day. TLC (ether-hexane, 2:1) then revealed that 7 had disappeared and that a new compound was present. Neutralisation with Amberlite IR-120 (H^+) (15 mL) and concentration of the solvent gave a residue (2.1 g) that was subjected to column chromatography (ether-hexane, 3:1) to afford syrupy 9 (1.42 g, 97%), $[\alpha]_D$ +2° (c, 0.8); IR (film) 3440 (OH), 3060, and 3025 (C-H, aromatic), 2980, 2925, and 2880 (C-H), 1495 and 1455 (benzyl), 1380 and 1370 (CMe_2), 1235, 1200, 1090, 1065, and 840 (1,3-dioxolane ring and C-O-C), and 695 cm^{-1} (aromatic); ^1H NMR δ 7.35 (s, 5, $CH_2\underline{Ph}$), 4.62 (s, 2, $\underline{CH_2}Ph$), 4.39 (broad s, 1, H-4), 4.29 (d, 1, H-3, $J_{3,4}$ = 3 Hz), 3.96-3.82 (m, 3, H-5,6,6'), 4.83 (d, 1, H-1, $J_{1,1'}$ = 11 Hz), 3.71 (d, 1, H-1'), 2.95 and 2.50 (2 broad s, 2, HO-1,4), 1.55 and 1.40 (2 s, 6, CMe_2).

Partial benzoylation of 9 (1.28 g, 4.1 mmol) in cooled (-10°) dry pyridine (6 mL) with benzoyl chloride (0.78 g, 5.6 mmol) and work-up of the reaction mixture as usual gave 5 (1.4 g, 83%).

Synthesis of 1-O-benzoyl-5-O-benzyl-2,3-O-isopropylidene-β-D-tagatopyranose (11) from 5. To a stirred mixture of anhydrous dimethylsulfoxide (1 g, 12.8 mmol) in dichloromethane (5 mL) at -78° was added a solution of trifluoroacetic acid anhydride (2 g, 9.5 mmol) in dichloromethane (2 mL) followed after 10 min, by a solu-

tion of 5 (1.08 g, 2.61 mmol) in dichloromethane (3 mL). Stirring was continued at -78° for 2 h, and then at room temperature overnight. Triethylamine (2.3 mL) was added and after 30 min, ether (40 mL) was added. The organic solution was washed with 10% aqueous hydrochloric acid, 10% aqueous sodium carbonate, water, and concentrated to give a residue that was purified by column chromatography (ether-hexane, 1:2) to afford 1-O-benzoyl-5-O--benzyl-2,3-O-isopropylidene- β -D-threo-2,4-hexodiulo--2,6-pyranose (10, 630 mg). Although 10 could not be obtained in pure state, however its ^{1}H NMR and IR spectra showed significant changes which indicated that oxidation had occurred.

To a cooled (~0°) solution of 10 (880 mg) in anhydrous methanol (20 mL) sodium borohydride (100 mg) was added. The mixture was left at room temperature for 2 h. TLC then showed the presence of 5 together with a new product. Neutralisation with acetic acid and concentration gave a residue that was extracted with chloroform (30 mL). The chloroform solution was concentrated and the obtained residue subjected to column chromatography (ether-hexane, 2:3) to yield 5 (260 mg) and 11 (235 mg, 37%) as a colourless syrup, $[\alpha]_D$ -43° (c, 0.84); IR (film) 3500 (OH), 3075 and 3040 (C-H, aromatic), 3000, 2950, and 2910 (C-H), 1730 (benzoate C=O), 1605 and 1590 (benzoate C=C), 1500 and 1455 (benzyl), 1380 (CMe_2), 1275 (benzoate C-O), 1220, 1115, 1075, and 840 (1,3-dioxolane ring and C-O-C), 750, 720, and 700 cm^{-1} (aromatic); ^{1}H NMR δ 8.10-8.00 and 7.65-7.28 (2 m, 5, relative intensity 2:3, Bz), 7.35 (s, 5, CH_2Ph), 4.71 (d, 1, H-1, $J_{1,1'}$ = 12 Hz), 4.61 (d, 1, H-1'), 5.51 (d, 1, H-3, $J_{3,4}$ = 2.8 Hz), 4.49 (s, 2, CH_2Ph), 4.18 (dd, 1, H-6, $J_{5,6}$ = 5.6, $J_{6,6'}$ = 12.5 Hz), 4.01 (dd, 1, H-4, $J_{4,5}$ = 7 Hz), 3.83 (dd, 1, H-6', $J_{5,6'}$ = 2.8 Hz),

3.80 (m, 1, H-5), 2.30 (broad s, 1, HO-4), 1.60 and 1.40 (2 s, 6, CMe_2).

1-O-Benzoyl-2,3-O-isopropylidene-β-D-tagatopyranose (12). To a solution of 11 (615 mg, 1.49 mmol) in methanol) (50 mL) was added palladium oxide (150 mg) and hydrogenated at ~1.5 atm for 1 day. TLC (ethyl acetate) then showed that 11 had disappeared and that a compound of lower mobility (R_f 0.61) was present. The catalyst was filtered off and the filtrate concentrated to a residue that was chromatographied (ether) to yield syrupy 12 (375 mg, 78%), $[\alpha]_D$ -3.4° (c, 1.2); IR (film) 3421 (OH), 3072 (C-H, aromatic), 2993 and 2944 (C-H), 1727 (benzoate C=O), 1604 and 1586 (benzoate C=C), 1382 (CMe_2), 1271 (benzoate C-O), 1216, 1109, 1072, and 870 (1,3-dioxolane ring and C-O-C), and 711 cm^{-1} (aromatic); ^1H NMR (80 MHz) δ 8.12-7.95 and 7.70-7.35 (2 m, 5, relative intensity 2:3, Bz), 4.48 (s, 2, 2 H-1), 4.42 (d, 1, H-3, $J_{3,4}$ = 2.5 Hz), 4.29-3.50 (m, 6, H-4,5,6,6′, and HO-4, 5), 1.55 and 1.35 (2 s, 6, CMe_2).

2,3-O-Isopropylidene-β-D-tagatopyranose (13). Compound 12 (350 mg, 1.08 mmol), was debenzoylated in anhydrous methanol (10 mL) with 1N sodium methoxide (1 mL) for 1 h. Work-up of the reaction mixture as above gave a residue that was subjected to column chromatography (ethyl acetate) to afford crystalline 13 (235 mg, quantitative), R_f 0.26 (ethyl acetate), mp 114-116°, $[\alpha]_D$ -43° (c, 1, methanol), IR (KBr) 3322 (OH), 2992, 2944, and 2880 (C-H), 1461, 1383 (CMe_2), 1266, 1215, 1111, 1062, 1044, 987, 976, 892, and 867 cm^{-1}; ^1H NMR (80 MHz) δ (acetone-d_6) 4.42 (d, 1, H-3, $J_{3,4}$ = 2 Hz), 4.22-3.37 (m, 9, H-1,1′,4,5,6,6′, and HO-1,4,5), 1.45 and 1.31 (2 s, 6, CMe_2).

Anal. Calc. for $C_9H_{16}O_8$: C, 49.08; H, 7.32. Found: C, 49.23; H, 7.15.

Acetonation of 13. A solution of 13 (190 mg, 0.86 mmol) in dry acetone (20 mL) and conc. sulfuric acid (0.05 mL) was stirred at room temperature with anhydrous copper sulfate (600 mg) for 1 day. TLC then showed one spot which had the same mobility (R_f 0.55) as an authentic sample of 1,2:3,4-di-O-isopropylidene-α-D-tagatofuranose (14). The mixture was neutralised (K_2CO_3), filtered, and concentrated. The residue was subjected to column chromatography (ether-hexane, 1:1) to give 14 (155 mg, 70%), mp 64-65°; $[\alpha]_D$ +79° (c, 2, acetone) [lit.[7] mp 65-66°, $[\alpha]_D$ +81.5° (c, 2, acetone)]; IR (KBr) 3525 (OH), 2994 and 2957 (C-H), 1380 and 1376 (CMe_2), 1260, 1168, 1079, 1062, 1034, 930, and 840 cm^{-1}; ^1H NMR (80 MHz) δ 4.83 (dd, 1, H-4, $J_{3,4}$ = 6, $J_{4,5}$ =3.5 Hz), 4.60 (d, 1, H-3), 4.22 (d, 1, H-1, $J_{1,1'}$ = 9 Hz), 4.03 (d, 1, H-1'), 4.00-3.75 (m, 3, H-5,6,6'), 2.34 (broad s, 1, HO-6), 1.44, 1.40, 1.38, and 1.29 (4 s, 12, 2 CMe_2).

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