Branched-chain 2-deoxy sugars. V. Application of the Wittig reaction to methyl 3,4-*O*-isopropylidene-β-D-*erythro*-pentopyranosid-2-ulose and attempted synthesis of nucleosides of 2-deoxy-2-*C*-methylpentoses

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Oxidation of methyl 3,4-*O*-isopropylidene-β-D-arabinopyranoside (**1**) with ruthenium tetroxide afforded methyl 3,4-*O*-isopropylidene-β-D-*erythro*-pentopyranosid-2-ulose (**2**) in 78% yield. Condensation of methylenetriphenylphosphorane with **2** in the presence of *n*-butyllithium yielded methyl 3,4-*O*-isopropylidene-2-deoxy-2-*C*-methylene-β-D-*erythro*-pentopyranoside (**3**) in 55% yield. Reduction of the latter with 10% palladium-on-charcoal gave a 7:1 mixture of two isomeric 2-deoxy-2-*C*-methylpentoside derivatives in 95% yield: the preponderant product had the D-*ribo* configuration. The fully blocked methyl glycosides were de-isopropylidenated with methanolic hydrogen chloride to yield **6** and **7** and these were converted into the *p*-toluoyl esters (**8**) and (**9**). Attempts to utilize the latter in the synthesis of nucleosides of 2-deoxy-2-*C*-methyl pentoses were unsuccessful.

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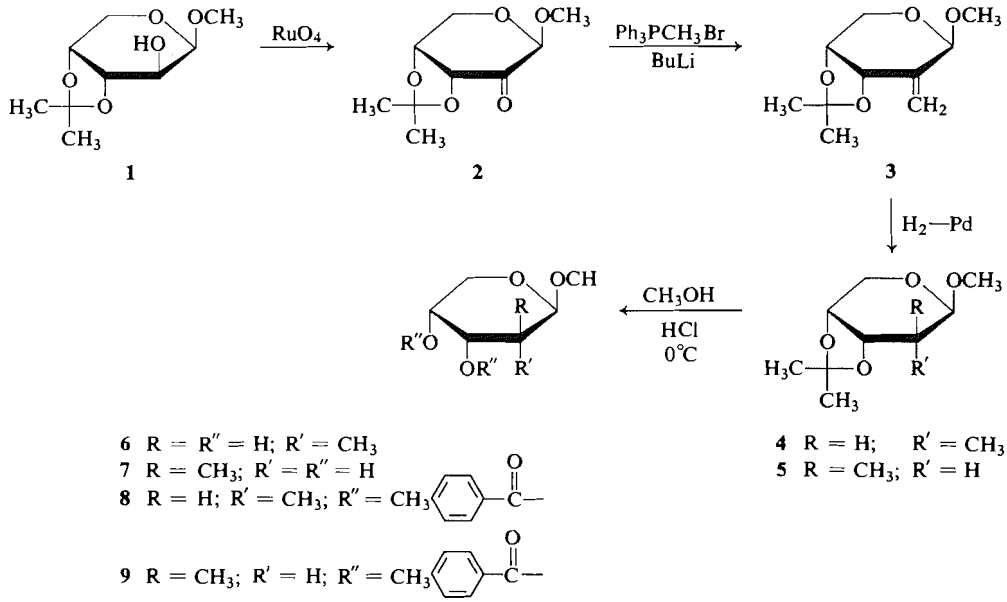
Introduction

Until 1967 there were few useful synthetic routes for the preparation of branched-chain deoxy sugars possessing a hydrogen and a *C*-alkyl, hydroxyalkyl, or aminoalkyl substituent on the same carbon (1–3). During the past few years the Wittig reaction has been successfully applied to several 3-keto sugar derivatives to afford unsaturated sugar derivatives; the latter have been readily converted stereoselectively in high yield into the aforementioned type of branched-chain deoxy sugars (4–7). There is also a report of a light-induced addition of 1,3-dioxolan to an unsaturated carbohydrate in the presence of acetone to afford a branched-chain sugar (8). Although sodium cyanide and hydrogen cyanide have been used to open carbohydrate epoxides (9, 10), and the oxo reaction has been applied to unsaturated carbohydrates (11) to afford branched-chain sugars, these routes give complex mixtures of products. A more promising supplementary route to the branched-chain amino sugars has been provided via the nitromethane addition to keto sugar derivatives and the nitroethane addition to dialdehydo sugar derivatives (12).

In continuation of our studies on the synthesis of branched-chain sugars and their subsequent utilization in the preparation of 3′-deoxy-3′-*C*-methyl (and hydroxyalkyl) sugar nucleosides (6, 13) we now wish to report an extension of the Wittig reaction to a 2-keto sugar derivative to afford two novel isomeric 2-*C*-methylpentoside derivatives.

Results and Discussion

Oxidation of methyl 3,4-*O*-isopropylidene-β-D-arabinopyranoside (**1**) with ruthenium tetroxide, according to a slight modification of the procedure of Lawton *et al.* (14), afforded methyl 3,4-*O*-isopropylidene-β-D-*erythro*-pentopyranosid-2-ulose (**2**) (see Scheme 1), which was obtained as the hydrate in crystalline form in 78% yield. Distillation of anhydrous benzene from the hydrate converted the latter into the keto sugar (**2**). Methyl 3,4-*O*-isopropylidene-β-L-*erythro*-pentopyranosid-2-ulose has been prepared by ruthenium tetroxide oxidation of the appropriate glycoside in 40% yield (15), whereas the D-enantiomer of the latter was prepared in 80% yield (16). Treatment of **1** with methylsulfoxide – phosphorus pentoxide (17) as oxidant gave a 40% yield of the keto sugar (**2**); utilization of methyl sulfoxide – acetic anhydride as oxidant (18) raised the yield to 55%. Reaction of methyltriphenylphosphonium bromide with *n*-butyllithium in hexane (19) with the 2-keto sugar (**2**) afforded the branched-chain unsaturated sugar, methyl 3,4-*O*-isopropylidene-2-deoxy-2-*C*-methylene-β-D-*erythro*-pentopyranoside (**3**), in 55% yield. Contaminants accompanying **3** were removed by chromatography on silica gel, with 10:1 benzene – ethyl acetate as eluent. The unsaturated sugar (**3**) was stable and could be distilled under reduced pressure. Substitution of tetrahydrofuran for ether as solvent in the Wittig reaction led to a significant decrease in yield of **3** and also led to partial degradation of the product. When methylenetriphenylphos-



SCHEME 1

phorane was obtained by allowing methyltriphenylphosphonium bromide in methyl sulfoxide to react with sodium hydride, according to a previously published procedure (6), then **3** was obtained in 3% yield.

Hydrogenation of the unsaturated sugar (**3**), with 10% palladium-on-charcoal as catalyst, gave a 7:1 mixture of *ribo* and *arabino* epimers, namely, methyl 2-deoxy-2-*C*-methyl-3,4-*O*-isopropylidene-β-D-*ribo* (**4**) and *arabino* (**5**) pyranoside in a combined yield of 95%. This mixture was separated by silica gel column chromatography with 50:1 benzene – ethyl acetate as developer. When Wilkinson catalyst (20) (triphenylphosphine ruthenium chloride) was used as catalyst, a 7:4 mixture of 2-*C*-methylribo- (**4**) and -arabinopentosides was obtained. The structures of **4** and **5** were readily deduced from their n.m.r. spectra in chloroform-*d*. The *ribo*-isomer (**4**) showed a 1-proton doublet at τ 5.62 with $J = 8$ Hz, which collapsed to a singlet on irradiation of H-2 at τ 8.3, that was assigned to H-1. The large geminal coupling of the axial anomeric hydrogen with the C-2 hydrogen indicates strongly that H-2 must be in an axial orientation, and therefore, the C-2 methyl group is in an equatorial orientation and **4** must be the *ribo*-isomer. On the other hand, the n.m.r. of **5** showed a 1-proton doublet at τ 5.51 with $J = 3$ Hz. The much smaller $J_{1,2}$ of compound **5** than of compound **4**, indicates that H-2 of **5** must be in an equatorial orientation, and therefore compound **5** must be methyl 2-deoxy-3,4-*O*-isopropylidene-β-D-arabinopyranoside.

Hydrolysis of **4** and **5** to afford the branched-chain methyl glycosides **6** and **7** posed a problem of unexpected difficulty. Hydrolysis of **4** and **5** with about 0.01 *M* hydrogen chloride in anhydrous methanol must be done under careful surveillance by t.l.c. monitoring. For optimal yield of product, the reaction mixture was kept at 0° for 2 h. Purification of the product was achieved by silica gel column chromatography with 10:1 benzene – ethyl acetate as eluent. Utilization of Dowex 50 (H^+) resin in methanol for removal of the isopropylidene group gave a mixture of at least four products which could not be separated by column chromatography. Complete hydrolysis of **4** and **5** was achieved in 5 min with 90% trifluoroacetic acid to afford 2-deoxy-2-*C*-methyl-D-*ribo*-(and *arabino*)pentose as evidenced by their n.m.r. spectra. The free sugars were accompanied by impurities which could not be removed and as a consequence no attempt was made to characterize the free sugars.

As the primary objective of the research outlined herein was to prepare 2′-*C*-methyl pyranosyl (and furanosyl) nucleosides, the next step was the

conversion of the methyl glycosides **6** and **7** into suitably blocked pyranosyl sugar halides. When the *p*-nitrobenzoyl group was used as a blocking group the *p*-nitrobenzoates of sufficient analytical purity for nucleoside synthesis could not be obtained. Treatment of **6** and **7** with *p*-toluoyl chloride in pyridine afforded the *p*-toluoyl esters **8** and **9** (crystalline) which appeared to have the correct structure (as judged from their n.m.r. spectra) but which gave elemental analysis which deviated slightly from the theoretical values (about 1%). These toluoyl esters were allowed to react with hydrogen bromide or hydrogen chloride in methylene chloride to afford the pyranosyl halide which was immediately allowed to react with 6-benzamidochloromercuripurine by an already published procedure (21) to afford a mixture of products. This mixture, after the usual work-up, was partially separated by preparative silica gel G t.l.c. with 1:1 benzene – ethyl acetate as developer to afford trace quantities of impure 2′-deoxy-2′-*C*-methylribo-β(and α)pyranosyl adenine nucleosides. The great difficulty in obtaining sufficient quanties of nucleosides for analysis and the recent publication (22) of nucleosides from 2-*C*-methyl-2-deoxy-*erythro*-D-pentose led us to abandon further work on the project.

Experimental

General considerations were similar to those previously described (6, 13).

Methyl 3-4-O-Isopropylidene-β-D-arabinopyranoside (1)

The title compound (**1**) was prepared from D-arabinose in 59% yield, b.p. 94° (at 0.75 mm pressure); $[\alpha]_D^{22}$ −202° (*c* 1, chloroform), according to a procedure used for the preparation of the L-enantiomer (23, 24), and agrees with the physical constants given for the enantiomer.

Methyl 3,4-O-Isopropylidene-β-D-erythro-pentopyranosid-2-ulose (2)

To a solution of methyl 3,4-*O*-isopropylidene-β-D-*arabino*-pyranoside (**1**) (4 g) in carbon tetrachloride (75 ml) was added water (15 ml), sodium hydrogen carbonate (1 g), and ruthenium dioxide (80 mg). Sodium metaperiodate (1.2 equiv of 5% aqueous solution) was added dropwise in small aliquots to the vigorously stirred solution (it is important to avoid adding excess of oxidant and to add the oxidant only when the color of the solution changes). After any excess oxidant was destroyed, by the addition of a few drops of isopropyl alcohol, the precipitated ruthenium compound was removed by filtration. The water layer was then extracted with chloroform (7 × 30 ml). This combined extract was now added to the carbon tetrachloride layer and evaporated to yield 3.2 g (78%) of the hydrate of the ketose (**2**). Recrystallization of this hydrate from methanol afforded 2.8 g of the ketose hydrate, m.p. 114°; $[\alpha]_D^{22}$ −161° (*c* 1, ethanol); ν(Nujol) 3600 (OH). The hydrate was converted to the ketose **2** by distilling benzene from it; ν(Nujol) 1750 (carbonyl).

When **1** was oxidized with methyl sulfoxide in the presence of phosphorus pentoxide (17) the yield of ketose (**2**) was 40%. Compound **1** was also converted into **2** in 55% yield using methyl sulfoxide – acetic anhydride as oxidant (18).

Application of the Wittig Reaction to 2 to Yield Methyl 3,4-O-Isopropylidene-2-deoxy-2-C-methylene-β-D-erythro-pentopyranoside (3)

Methyltriphenylphosphonium bromide (10.95 g) was added in small portions with stirring to a solution of *n*-butyllithium in hexane (13.2 ml of 2.25 *M*) and ether (50 ml) contained in a nitrogen-filled dry box. After the reactants were stirred for 4 h, a solution of the ketose (**2**) (6 g dissolved in 50 ml of ether) was added dropwise to the ylide and the reaction allowed to proceed for an additional 2 h. The reaction mixture was filtered and the filtrate extracted with water (3 × 10 ml) until the last aqueous extract was neutral. The combined ether extracts were dried with magnesium sulfate, filtered, and the filtrate evaporated to a syrup (3.3 g, 55%). Silica gel column chromatography of this syrup with 10:1 benzene – ethyl acetate as developer gave 1.7 g of pure unsaturated sugar **3**. The analytical sample was prepared by distillation at 80° at 0.005 atm pressure; $[\alpha]_D^{22}$ −176° (*c* 2, chloroform); τ ($CDCl_3$) 4.6 (m, methylene group), 4.9 (t, H-1), 5.2 (d, H-3), 5.8 (d, H-4), 6.2 (d, H-5), 6.55 (s, OCH_3), 8.5 (d, CMe_2).

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.00; H, 8.07. Found: C, 60.12; H, 8.14.

When the ketose **2** was allowed to react with the same ylide in methyl sulfoxide containing sodium hydride according to a previously published procedure (6), then a 3% yield of **3** was obtained. Use of *n*-butyllithium in tetrahydrofuran led to considerable cleavage of the glycosidic bond of **2**.

Hydrogenation of 3 to Yield Methyl 2-Deoxy-2-C-methyl-3,4-O-isopropylidene-β-D-ribopyranoside (4) and Methyl 2-Deoxy-2-C-methyl-3,4-O-isopropylidene-β-D-arabinopyranoside (5)

(a) Using Pd–C as Catalyst

The unsaturated sugar **3** (0.4 g) in 20 ml of methanol was hydrogenated using 10% palladium-on-charcoal as catalyst; 1 mol equiv of gas was absorbed in 1 h. The catalyst was removed by filtration through Celite and the filtrate was then evaporated to a syrup (0.38 g, 95%). The ratio of isomers **4** and **5** was 7:1 as evidenced by n.m.r.

The mixture of isomers **4** and **5** (2.65 g) was separated by chromatography on silical gel (40 g, activity grade II) with 50:1 benzene – ethyl acetate as developer. The slower moving zone (1.61 g, *ribo*-pentoside (**4**)) had an R_f 0.50 with 10:1 benzene – ethyl acetate as developer and a b.p. of 60–65° at 12 mm pressure; $[\alpha]_D^{22}$ −81° (*c* 2, chloroform); τ ($CDCl_3$) 5.62 (d, H-1, $J_{1,2}$ = 8 Hz), 5.8 (m, one H), 6.35 (m, two H), 6.6 (s, OCH_3), 8.3 (m, H-2), 8.6 (CMe_2), 8.85 (d, J = 6 Hz, Me-2).

Anal. Calcd. for **4**, $C_{10}H_{18}O_4$: C, 59.40; H, 8.97. Found: C, 59.34; H, 9.06.

The faster moving zone (0.32 g of *arabino*-pentoside (**5**) had an R_f 0.55 and b.p. of 60–65° at 12 mm pressure; $[\alpha]_D^{22}$ −78° (*c* 2, chloroform); τ ($CDCl_3$) 5.5 (d, H-1, $J_{1,2}$ = 3 Hz), 5.9–6.3 (m, equal to 4H), 6.65 (s, OCH_3), 8.2 (m, H-2), 8.55 (d, CMe_2), 8.95 (d, J = 6.5 Hz, Me-2). For analysis **5** was distilled under reduced pressure.

Anal. Calcd. for **5**, $C_{10}H_{18}O_4$: C, 59.40; H, 8.91. Found: C, 59.30; H, 9.02.

(b) Using Triphenylphosphine Ruthenium Chloride (Wilkinson Catalyst)

The unsaturated sugar **3** (0.66 g) was dissolved in benzene (50 ml) and hydrogenated in the presence of triphenylphosphine ruthenium chloride (0.2 g) (20) at 20° at atmospheric pressure for 3 days. After the solvent was removed under reduced pressure, petroleum ether (20 ml, b.p. 30–60°) was added. The precipitate was removed by filtration, washed with petroleum ether (2 × 10 ml), and the filtrate evaporated under reduced pressure to yield 0.60 g (91%) of a 7:4 mixture of the isomers **4** and **5**.

*Partial Hydrolysis of **4** to Yield Methyl 2-Deoxy-2-C-methyl-β-D-ribopyranoside (**6**)*

Methyl 3,4-*O*-isopropylidene-2-deoxy-2-*C*-methyl-β-D-ribopyranoside (**4**) (0.32 g) was dissolved in an ice-cold solution of 5 ml anhydrous methanol containing 0.01 *M* anhydrous hydrogen chloride. After the reaction mixture was kept at 0° for 2 h, it was neutralized with an excess of solid sodium hydrogen carbonate, filtered, and the filtrate evaporated to yield a syrup (0.22 g, 87%). This syrup was chromatographed on 20 g silica gel (activity grade II) with 10:1 benzene – ethyl acetate as developer to afford 0.181 g of a homogeneous powder (by t.l.c.), R_f 0.25 on silica gel G with 10:1 benzene – ethyl acetate as developer; $[\alpha]_D^{22}$ −151° (*c* 1, chloroform); τ ($CDCl_3$) 5.6 (d, H-1, $J_{1,2}$ = 8 Hz), 6.1–6.5 (m, H-5, H-4, H-3), 6.6 (OCH_3), 7.2 (s, OH), 8.3 (m, H-2), 8.9 (d, J = 7 Hz, CH_3).

*Methyl 2-Deoxy-2-C-methyl-β-D-arabinopyranoside (**7**)*

The arabino sugar **5** (0.100 g) was partially hydrolyzed according to the same procedure used for the hydrolysis of **4**. The product was, however, not purified by column chromatography but was crystallized from petroleum ether (b.p. 30–60°) to give 0.054 g (67%) of crystalline methyl 2-deoxy-2-*C*-methyl-β-D-arabinopyranoside, R_f 0.7 with 10:1 benzene–ethyl acetate as developer; m.p. 136°; $[\alpha]_D^{22}$ − 24° (*c* 2, chloroform); τ ($CDCl_3$) 5.45 (d, H-1, $J_{1,2}$ = 3 Hz), 6.0–6.5 (m, H-5, H-4, H-3), 6.65 (s, OCH_3), 8.0 (s, OH, overlapping H-2), 7.8–8.2 (m, H-2), 9.0 (d, J = 7 Hz, CH_3).

Anal. Calcd. for $C_7H_{14}O_4$: C, 51.84; H, 8.70. Found: C, 51.66; H, 8.67.

*Attempted Complete Hydrolysis of Sugars **4** and **5** with Trifluoroacetic Acid to Yield 2-Deoxy-2-C-methyl-D-ribo-pentose and 2-Deoxy-2-C-methyl-D-arabino-pentose*

The blocked *ribo*-isomer **4** (0.49 g) was allowed to react at room temperature for 5 min with 90% trifluoroacetic acid (5 ml). The solution was immediately evaporated at 30° at 1 mm pressure. The syrup was triturated with ether and the white precipitate was isolated by decantation, yield 0.35 g. The main component had $R_{Glucose}$ 1.7 on paper with 8:2:2 ethyl acetate – pyridine – water as developer (several additional spots were visible). The sugar gave a positive Fehling's test. τ (D_2O) of the *ribo* free sugar 4.8–5.3 (m, H-1, poorly resolved), 5.5–6.7 (m, H-5, H-4, H-3), 7.5–8.3 (m, H-2), 8.8–9.1 (three d, CH_3). The free sugar was probably a mixture of α- and β-anomers of both pyranose and furanose sugars.

Similar treatment of the *arabino*-isomer (**5**) gave mainly one reducing sugar having $R_{Glucose}$ 1.7 which in D_2O solution probably existed as an anomeric mixture of pyranose and furanose sugars.

*Methyl 2-Deoxy-2-C-methyl-3,4-di-O-p-toluoyl-β-D-ribopyranoside (**8**)*

To an ice-cold solution of compound **6** (0.282 g) in anhydrous pyridine (8 ml) was added with mixing freshly distilled *p*-toluoyl chloride (0.5 ml). After the reaction mixture stood overnight at room temperature, water (10 ml) was added, and then the mixture was extracted with chloroform (3 × 15 ml). The combined chloroform extracts were washed with saturated aqueous sodium hydrogen carbonate, water, dried with magnesium sulfate, filtered, and the filtrate evaporated under reduced pressure to yield a syrup (0.65 g). This syrup was chromatographed on 50 g silica gel (grade II) with 50:1 benzene – ethyl acetate as developer to afford chromatographically pure **8** (0.530 g, 73%), R_f 0.7 (10:1 benzene – ethyl acetate); $[\alpha]_D^{22}$ −62° (*c* 1, chloroform); τ ($CDCl_3$) 2.0 (m), 2.7 (m), 4.22 (t, equal to one H), 4.55 (m, equal to one H), 5.35 (d, H-1, $J_{1,2}$ = 6 Hz), 5.9 (m, equal to three H), 6.45 (s, OCH_3), 7.6 (d, toluoyl CH_3), 2.1 (m, H-2), 8.8 (d, *C*—$2CH_3$, J = 7 Hz).

*Methyl 2-Deoxy-2-C-methyl-3,4-di-O-p-toluoyl-β-D-arabinopyranoside (**9**)*

The arabinopyranoside **7** was allowed to react with *p*-toluoyl chloride in the same manner as described for the preparation of **8** to afford **9** in 69% yield. Compound **9** was recrystallized from methanol–ether, m.p. 84–85°; R_f = 0.7; $[\alpha]_D^{22}$ −69° (*c* 1, chloroform); τ ($CDCl_3$) 2.0 (m), 2.7 (m), 4.45 (t, equal to one H), 4.6 (d, equal to one H), 5.23 (d, H-1, $J_{1,2}$ = 3 Hz), 5.95 (m, equal to two H), 6.58 (s, OCH_3), 7.6 (d, toluoyl CH_3), 8.7 (m, H-2), 8.95 (d, *C*—$2CH_3$, J = 7 Hz). The elemental analysis of **9** deviated by about 1% from the theoretical values, but the n.m.r. spectrum of **9** was in complete accord with the title compound.

Attempted Synthesis of 9-(2′-Deoxy-2′-C-methyl-β-(and α)-D-arabino(and ribo)pyranosyl)adenine

The blocked methyl arabinopyranoside (**9**) was converted into the blocked pyranosyl bromide by reaction with hydrogen bromide in methylene chloride at 0° and subsequently immediately condensed with 6-benzamidochloromercuripurine in the presence of cadmium carbonate according to a procedure already published (21). A mixture of α- and β-blocked nucleosides as syrups was obtained in very low yield having R_f of 0.4 and 0.3 on silica gel G with 1:1 benzene–ethyl acetate as developer; $[\alpha]_D^{22}$ (faster component) −94° (*c* 0.2 chloroform), $[\alpha]_D^{22}$ (slower component) −62° (*c* 0.2, chloroform); τ ($CDCl_3$) (faster component) 3.6 (d, probably H-1′, $J_{1',2'}$ = 3 Hz), 7.5 (d, *p*-toluoyl CH_3),

8.95 (d, C-2′-CH_3, J = 7 Hz); τ ($CDCl_3$) (slower component) 4.15 (d, probably H-1′, $J_{1',2'}$ = 1.5 Hz), 7.6 (d, *p*-toluoyl CH_3), 9.3 (d, C-2′-CH_3, J = 7 Hz).

Insufficient quantity of nucleosides was obtained for satisfactory analyses.

Attempts to use the blocked methyl ribopyranoside (**8**) as an intermediate in the nucleoside synthesis gave only trace amounts of nucleosides. Attempts to convert the *p*-nitrobenzoyl esters of **6** and **7** into nucleosides were also unsuccessful.

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