Alternative syntheses of methylated sugars. XI.* 2,4-Di-*O*-methyl- and 3,4-di-*O*-methyl-D-xylopyranose

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2-*O*-Benzyl- and 3-*O*-benzyl-D-xylose, intermediates bearing nonmigratory substituents important in carbohydrate syntheses, have been prepared. Treatment of these with methanolic hydrogen chloride gave crystalline methyl glycopyranosides, which, upon methylation and removal of the blocking groups, yielded 2,4-di-*O*-methyl- and 3,4-di-*O*-methyl-D-xylopyranose.

The title compounds have been reported to occur in the fission products of certain aldouronic acids [1—6] and wood saponins [7]. 2,4-Di-*O*-methyl-D-xylopyranose was previously obtained by partial methylation of methyl α,β-D-xylopyranoside [8] and methyl β-D-xylopyranoside [9] followed by acid hydrolysis. 3,4-Di-*O*-methyl-D-xylopyranose was synthesized from D-arabinose [10] and, albeit in moderate yield, from methyl 2-*O*-benzoyl-3,5-isopropylidene-α,β-D-xylofuranoside by methanolysis, methylation, debenzoylation, and hydrolysis. This approach [11, 12] presumed the change of a furanose to pyranose ring during methanolysis.

Here we describe alternative routes leading to 2,4-di-*O*-methyl- and 3,4-di-*O*-methyl-D-xylopyranose using intermediates bearing nonmigratory benzyl group for masking the positions C_3—OH and C_2—OH, respectively. The final sugar derivatives and their methyl glycosides described here are useful reference compounds in methylation analysis of poly- and oligosaccharides containing D-xylose as a structural unit.

Experimental

Melting points were determined on a Kofler hot stage. Optical rotations were measured with a Bendix—Ericsson Model 143 A automatic polarimeter. Thin-layer chromatography (TLC) on Silica gel G coated glass slides and column chromatography on silica gel (0.05—0.1 mm) was performed with: *A*. benzene—ethyl acetate 4 1, *B*. chloroform—acetone 10 1, *C*. heptane—acetone 8 1, *D*. chloroform—acetone 9 2, *E*. benzene—acetone 10 1, *F*. chloroform—methanol 8 1, *G*. ether—benzene 10 1, and *H*. chloroform—acetone 4. The solvent ratios are based on volumes. The components were located by spraying with 5% sulfuric acid in ethanol and heating until permanent char spots were visible. The solutions were concentrated on a rotary evaporator at <40°C. 1,2-Dimethoxyethane was dried as described by *Perrin et al.* [13] and stored over sodium hydride.

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3-O-Benzyl-D-xylose (I)

To a stirred solution of 3-*O*-benzyl-1,2-*O*-isopropylidene-5-aldehydo-α-D-xylo-pentodialdo-1,4-furanose [14] (38 g) in cold (<0°C) dry ether (500 ml) a suspension of lithium aluminium hydride (5 g) in dry ether was added portionwise. The mixture was stirred for another ten minutes and TLC (in solvent *A*) showed then complete conversion of the starting material (R_F 0.5) into one product (R_F 0.3). The excess of the reducing agent was decomposed with continued stirring and cooling by the addition of water (500 ml). The mixture was filtered and the solids were washed with chloroform. The filtrate combined with the washings were concentrated to remove the organic solvents and the water solution was adjusted to pH 8 by an addition of acetic acid. The sugar component was extracted with chloroform, concentrated, and vacuum distilled (b.p. 144—145°C/0.02 torr) to give chromatographically pure syrupy 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-xylofuranose (35 g, 89%).

A portion of the obtained product (33 g) in water (700 ml) was stirred with Dowex 50W (200—400 mesh), H^+ form (35 g) on a boiling water bath for 20 minutes at which time TLC in the system *A* showed that the hydrolysis was complete. The ion-exchanger was filtered, washed with hot water and the water solution was concentrated to dryness to give a crystalline residue. Recrystallization from ethyl acetate afforded 25 g (88.5%) of pure *I*, m.p. 120°C, $[\alpha]_D^{25}$ +26° (extrapolated) → +23.3° (2 min) → −11.2° (1 hr, const), (*c* 0.985, water).

For $C_{12}H_{16}O_5$ (240.25) calculated: 59.99% C, 6.71% H; found: 60.04% C, 6.76% H.

Methyl 3-O-benzyl-α-D-xylopyranoside (II)

Compound *I* (10 g) was treated under reflux and with exclusion of moisture with 2% methanolic hydrogen chloride (100 ml) for 6 hours. The solution was neutralized with lead carbonate, filtered and concentrated to give a crystalline residue (10.5 g, 99.3%). Crystallization from ethyl acetate gave 4.1 g (38.8%) of pure *II*, m.p. 133°C, $[\alpha]_D^{24}$ +116.2° (*c* 0.99, acetone).

For $C_{13}H_{18}O_5$ (254.27) calculated: 61.40% C, 7.13% H, 12.20% CH_3O; found: 61.44% C, 7.03% H, 12.70% CH_3O.

An addition of hexane to the mother liquor gave more crystalline product (3 g, 28.4%), a mixture of α and β anomers of methyl 3-*O*-benzyl-D-xylopyranoside, which was processed as described in the following paragraph.

Methyl 3-O-benzyl-2,4-di-O-methyl-α- and -β-D-xylopyranoside (III and IV)

To an ice-cold solution of methyl 3-*O*-benzyl-α,β-D-xylopyranoside (12.5 g) in 1,2-dimethoxyethane (130 ml) sodium hydride (4.8 g) was added portionwise with stirring. The cooling was removed and the mixture was stirred, with the exclusion of atmospheric moisture and carbon dioxide, for 15 minutes followed by the addition of methyl iodide (18.5 ml). After 30 minutes of continued stirring TLC in system *B* showed that the reaction was complete. Cautious addition of water (100 ml) was followed by the evaporation of the organic solvents and the oily product (R_F 0.8, *cf.* 0.3 for the starting material) was combined with the chloroform extract of the water layer. The chloroform solution was washed with water until neutral, dried with anhydrous sodium sulfate and concentrated to give 13.7 g (~100%) of a syrup which in the system *C* showed the presence of two components (R_F 0.3 and 0.4). Elution from a column of silica gel (80 4 cm) gave 3.8 g (27.8%) of the faster moving methyl 3-*O*-benzyl-2,4-di-*O*-methyl-

-β-D-xylopyranoside *IV*, m.p. 53°C (after repeated crystallization from *n*-heptane), $[\alpha]_D^{26}$ −37° (*c* 0.99, chloroform).

For $C_{15}H_{22}O_5$ (282.33) calculated: 63.81% C, 7.86% H, 32.98% CH_3O; found: 64.25% C, 7.95% H, 33.30% CH_3O.

The slower moving component was methyl 3-*O*-benzyl-2,4-di-*O*-methyl-α-D-xylopyranoside *III* (4.9 g, 35.8%) which was vacuum distilled (b.p. 111—112°C/0.015 torr) and collected as a colourless syrup having $[\alpha]_D^{26}$ +90.1° (*c* 1.04, chloroform). These physical constants were identical with those of the product obtained by methylation of *II*.

Found: 63.40% C, 7.81% H, 32.70% CH_3O.

An intermediate mixed fraction was also obtained.

Methyl 2,4-di-O-methyl-α- and -β-D-xylopyranoside (V and VI)

Compound *III* (4.5 g) dissolved in dry methanol (225 ml) was hydrogenated at room temperature over palladium-on-charcoal catalyst until the starting material disappeared from the reaction mixture as shown by TLC in the solvent system *B*. The product *V* (R_F 0.3, *cf.* 0.8 for the starting material) was isolated in the usual manner to give 3 g (~100%) of a syrup which had, after vacuum distillation (b.p. 76—77°C/0.02 torr) $[\alpha]_D^{26}$ +143° (*c* 1.07, chloroform).

For $C_8H_{16}O_5$ (192.21) calculated: 49.98% C, 8.39% H, 48.43% CH_3O; found: 49.55% C, 8.24% H, 48.54% CH_3O.

Catalytic hydrogenation of *IV* (2.95 g) under the conditions described above gave 1.9 g (96.4%) of methyl 2,4-di-*O*-methyl-β-D-xylopyranoside (*VI*) which crystallized from ether—hexane. Recrystallization from the same solvent gave material melting at 77—78.5°C. Ref. [9] gives m.p. 77.5—78.5°C.

2,4-Di-O-methyl-D-xylopyranose (VII)

The glycoside *VI* (1 g) was heated at 100°C in 5% hydrochloric acid (15 ml) for 30 minutes at which time TLC in the system *D* showed that the hydrolysis was practically complete. The solution was cooled to room temperature and neutralized (Ionenaustauscher II, OH^- form, Merck A. G., Darmstadt). Concentration and recrystallization of the crystalline residue from ether—ethyl acetate yielded 0.67 g (72.3%) of *VII* having m.p. 108—109°C, $[\alpha]_D^{26}$ −26° (extrapolated) → −19.3° (1.5 min) → −3.3° (5 min) → → +22° (50 min, const), (*c* 3, water). Ref. [7] gives m.p. 108°C and $[\alpha]_D$ −30° → +22° (water). Ref. [9] gives m.p. 116—118°C and $[\alpha]_D^{25}$ +9.4° (5 min) → +24.7° (50 min, const), (*c* 3, water).

2-O-Benzyl-D-xylose (VIII)

To a solution of methyl 3,5-*O*-isopropylidene-α,β-D-xylofuranoside [12] (16.4 g) in benzylchloride (16.5 ml) powdered potassium hydroxide (8.5 g) was added and the mixture was vigorously stirred for 30 minutes while the temperature was kept at 110°C. At this time TLC in the solvent system *E* showed that no starting material was present in the reaction mixture. Methyl 2-*O*-benzyl-3,5-*O*-isopropylidene-α,β-D-xylofuranoside (R_F 0.5 and 0.6, *cf.* 0.1 and 0.3 for the starting material) was isolated in the usual manner and collected, after vacuum distillation (b.p. 128—132°C/0.02 torr), as a colourless syrup (22 g, 93.3%) having $[\alpha]_D^{24}$ +22° (*c* 1.07, chloroform).

For $C_{16}H_{22}O_5$ (294.33) calculated: 65.29% C, 7.54% H, 10.54% CH_3O; found: 64.95% C, 7.42% H, 10.90% CH_3O.

The obtained product (21.5 g) and Dowex 50W (200—400 mesh), H^+ form (21.5 g) were heated in water (220 ml) with stirring at 80°C for 30 minutes and TLC in the solvent system *E* showed then complete disappearance of the starting material. One product was detected having the same chromatographic mobility (R_F 0.3, system *F*) as 3-*O*-benzyl-D-xylose which indicated that both the blocking groups were removed. The mixture was worked up as described in the preparation of *I* and compound *VIII* was crystallized from ethyl acetate. Yield 13.5 g (76.8%), m.p. 108—109°C, $[\alpha]_D^{25}$ +50° (extrapolated) → 46.5° (2.5 min) → +25.8° (2 hrs, const), (*c* 1.01, water).

For $C_{12}H_{16}O_5$ (240.25) calculated: 59.99% C, 6.71% H; found: 59.94% C, 6.65% H.

Methyl 2-O-benzyl-β-D-xylopyranoside (IX)

2-*O*-Benzyl-D-xylose (5.5 g) in 2% methanolic hydrogen chloride (55 ml) was heated under reflux for 22 hours and, after usual work-up, the obtained syrup (5.8 g, ~100%) was chromatographed on a column of silica gel (60 × 4.5 cm) using system *G*. The fastest moving component *IX* (R_F 0.3, system *G*) crystallized on concentration (1.9 g, 32.8%). Recrystallization from chloroform—*n*-heptane gave material melting at 90—90.5°C and having $[\alpha]_D^{24}$ −18° (*c* 1.02, chloroform).

For $C_{13}H_{18}O_5$ (254.27) calculated: 61.40% C, 7.13% H, 12.20% CH_3O; found: 61.15% C, 7.15% H, 12.19% CH_3O.

A mixture of methyl pyranosides and methyl furanosides of 2-*O*-benzyl-D-xylose, eluted subsequently, was processed as described below.

Methyl 2-O-benzyl-3,4-di-O-methyl-β-D-xylopyranoside (X)

Compound *IX* (1 g) was methylated under the conditions employed in the preparation of *III* and *IV*. The obtained syrup crystallized on cooling and pure *X*, recrystallized from hexane, had m.p. 59°C and $[\alpha]_D^{25}$ −22.8° (*c* 1.14, chloroform).

For $C_{15}H_{22}O_5$ (282.33) calculated: 63.81% C, 7.86% H, 32.98% CH_3O; found: 63.79% C, 7.85% H, 32.45% CH_3O.

Methyl 3,4-di-O-methyl-β-D-xylopyranoside (XI)

The fully substituted substance *X* (0.9 g) was hydrogenated at room temperature in methanol (50 ml) over palladium-on-charcoal catalyst and the reaction mixture was worked up in the usual manner. Chromatographically pure *XI* (0.6 g, 98%, R_F 0.3, system *B*, *cf.* 0.8 for the starting material) was obtained. After recrystallization from ether—hexane it had m.p. 88—89°C and $[\alpha]_D^{25}$ −74.2° (*c* 1.32, water). Ref. [10] gives m.p. 89—90°C and $[\alpha]_D^{19}$ −71° (*c* 1.53, water).

3,4-Di-O-methyl-D-xylopyranose (XII)

A. The glycoside *XI* (250 mg) was heated in 5% hydrochloric acid (4 ml) at 95°C for 1 hour and TLC (system *D*) showed then that the hydrolysis was almost complete. The solution was neutralized (Ionenaustauscher II, OH^- form, Merck A. G., Darmstadt), concentrated and the product (R_F 0.2, *cf.* 0.5 for the starting material) was purified by elution from a silica gel column (20 × 1.8 cm) using solvent *H*. The vacuum dried syrup (197 mg, 85%) had $[\alpha]_D^{25}$ +20.3° (*c* 1.28, methanol). Ref. [6] gives $[\alpha]_D^{25}$ +22.1° (*c* 0.7, methanol), and Ref. [1] gives $[\alpha]_D^{20}$ +31 ± 5° (*c* 0.57, methanol).

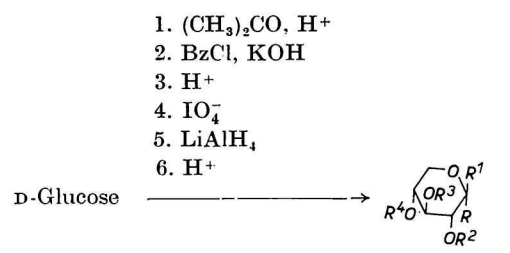
B. The mixture of methyl pyranosides and methyl furanosides obtained from the silica gel chromatography after separation of *IX* (3.7 g) was methylated and hydrogenated as described above. The product (2.3 g, 82%) showed the presence of two minor components having the same chromatographic mobility (R_F 0.25 and 0.5, system *B*) as authentic samples of methyl furanosides of 3,5-di-*O*-methyl-D-xylose [15] between which was located the major reaction product, the mixture of methyl pyranosides of 3,4-di-*O*-methyl-D-xylose (R_F 0.4). On careful heating, the individual compounds can be distinguished also according to the colour of the produced spots. Methyl furanosides of 3,5-di-*O*-methyl-D-xylose give two excellently separated brownish spots; methyl pyranosides of 3,4-di-*O*-methyl-D-xylose, located between them, do not separate one from another and give one dark violet spot.

The syrupy product (2.3 g), dissolved in 0.5 N sulfuric acid (45 ml) was heated with stirring at 50—60°C and the course of the hydrolysis was periodically checked by TLC which after one hour showed disappearance of methyl furanosides of 3,5-di-*O*-methyl-D-xylose from the reaction mixture and the presence of a new product — 3,5-di-*O*-methyl-D-xylose (R_F 0.1), while the intensity of the violet spot corresponding to the mixture of methyl pyranosides of 3,4-di-*O*-methyl-D-xylose remained practically unchanged. The hydrolyzate was neutralized with barium carbonate, filtered, concentrated and the resulting syrup was resolved on a column of silica gel (30 × 27 cm) using the solvent system *H*. The obtained mixture of methyl pyranosides of 3,4-di-*O*-methyl-D-xylose (2 g) was then hydrolyzed as described ad A, and the isolated 3,4-di-*O*-methyl-D-xylopyranose was collected as a pale yellow syrup (1.7 g, 66% based on 3.7 g of the starting mixture of methyl glycosides of 2-*O*-benzyl-D-xylose), $[\alpha]_D^{25}$ +26.5° (*c* 1.05, methanol). The substance was further purified by vacuum distillation (bath temperature 130°C/0.025 torr). The colourless product thus obtained had $[\alpha]_D^{24}$ +34.6° (*c* 1.01, methanol).

Discussion

Robertson and *Speedie* [11] described methyl di-*O*-methyl-D-xyloside (m.p. 61°C, $[\alpha]_D$ −82°) to which they attributed the methyl 2,4-di-*O*-methyl-β-D-xylopyranoside structure. They prepared this compound by a sequence of reactions involving first monotritylation of methyl β-D-xylopyranoside, acetylation of the other two hydroxyl groups, replacement of the trityl group by a nitrate group, deacetylation, methylation, and reductive removal of the nitrate group. None of the intermediates of this rather complicated procedure, except the diacetyl nitrate derivative, were crystalline and the physical constants of the final product disagreed with the constants of methyl 2,4-di-*O*-methyl-β-D-xylopyranoside (m.p. 77.5—78.5°C, $[\alpha]_D$ −70°) of *Wintersteiner* and *Klinsberg* [9]. As the latter synthesis [9] involved partial methylation, the product was thoroughly examined and the authors unequivocally showed that the methoxyl groups were present at the positions C_2 and C_4. This showed, at the same time, that previous procedure [11] did not give the desired product.

In the present work 2,4-di-*O*-methyl-D-xylopyranose is synthesized starting from 3-*O*-benzyl-D-xylose *I* which can be prepared in good yield by the reduction of the easily obtainable 3-*O*-benzyl-1,2-isopropylidene-5-aldehydo-α-D-xylo-pentodialdo-1,4-furanose [14] and following hydrolysis. Treatment of *I* with hot methanolic hydrogen chloride gave crystalline methyl 3-*O*-benzyl-α-D-xylopyranoside *II*. By a logical sequence of the reactions (see Experimental and Scheme 1) we obtained 2,4-di-*O*-methyl-D-xylopyranose *VII* of which the β form crystallized, the anomeric configuration being assigned on the basis of the change of the optical rotation during mutarotation (see Experimental).



	R	R^1	R^2	R^3	R^4
I	(H, OH)		H	Bz	H
II	OMe	H	H	Bz	H
III	OMe	H	Me	Bz	Me
IV	H	OMe	Me	Bz	Me
V	OMe	H	Me	H	Me
VI	H	OMe	Me	H	Me
VII	H	OH	Me	H	Me

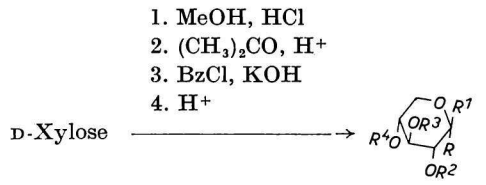
Me — methyl, Bz — benzyl.

Scheme 1

The physical constants of *VII* are in an excellent agreement with the values found by previous authors [7] who isolated the same substance from a natural source. The equilibrium rotation agrees well with that of the authors [9] who apparently obtained the α form of the sugar by an independent route.

The syntheses of 3,4-di-*O*-methyl-D-xylopyranose realized up to now have obvious drawbacks. The original synthesis [11], ambiguous in that migratory benzoyl group was used for protecting the C_2—OH position, was justifiably criticized [10]; an attempt to improve essentially the same procedure failed to give good yield of the desired product [12]. Better results were obtained [10] starting from D-arabinose which, however, is not a cheap comodity.

The fact that 2-*O*-benzyl-D-xylose *VIII* could be obtained in good yield from methyl 3.5-*O*-isopropylidene-α,β-D-xylofuranoside [12] by benzylation and subsequent hydrolysis made the substance *VIII* the logical starting material for the present approach to the synthesis of *XII*. As in the synthesis of 2,4-di-*O*-methyl-D-xylopyranose a non-migratory substituent could thus be used for masking the hydroxyl group which in the final product was to remain unsubstituted. Treatment of *VIII* with methanolic hydrogen chloride gave a mixture of methyl glycosides of which none could be obtained crystalline directly from this mixture by crystallization. The mixture apparently contained a relatively larger proportion of methyl furanosides than the mixture obtained by the same treatment of 3-*O*-benzyl-D-xylose. This should not be surprising since the other authors [16] observed that treatment with acidic methanol of a D-xylose derivative etherally substituted at C_2—OH results in an equilibrium mixture of methyl glycosides in which methyl furanosides are present in a relatively larger proportion compared to a similar mixture obtained by the same treatment of a C_3—OH etherally substituted D-xylose derivative. The methyl glycoside *IX* having the fastest chromatographic mobility could be, however, separated from this mixture by chromatography on silica gel and obtained in crystalline condition. Following the sequence described in the Experimental



	R	R^1	R^2	R^3	R^4
VIII	(H, OH)		Bz	H	H
IX	H	OMe	Bz	H	H
X	H	OMe	Bz	Me	Me
XI	H	OMe	H	Me	Me
XII	(H, OH)		H	Me	Me

Me — methyl, Bz — benzyl.

Scheme 2

(see also Scheme 2) 3,4-di-*O*-methyl-D-xylopyranose was obtained, the optical rotation of which agreed well with the values known in the literature [1, 6].

Preliminary experiments showed that the presence of methyl furanosides of 3,5-di-*O*-methyl-D-xylose in a mixture with methyl pyranosides of 3,4-di-*O*-methyl-D-xylose can be determined by TLC. Attempts were therefore made to utilize the syrupy mixture of methyl glycosides of 2-*O*-benzyl-D-xylose eluted from the silica gel column after separation of *IX* (see Experimental) for obtaining 3,4-di-*O*-methyl-D-xylopyranose. The mixture was methylated and debenzylated. The methyl furanosides of 3,5-di-*O*-methyl-D-xylose produced by methylation of methyl furanosides of 2-*O*-benzyl-D-xylose were converted by mild acid hydrolysis to 3,5-di-*O*-methyl-D-xylose, having much slower chromatographic mobility than any of the methyl glycosides present. 3,5-Di-*O*-methyl-D-xylose was then readily removed by chromatography on a column of silica gel. Using authentic standards of methyl furanosides of 3,5-di-*O*-methyl-D-xylose as reference compounds the course of partial hydrolysis was followed by TLC which eventually, under the conditions described (see Experimental) indicated complete disappearance of these substances from the reaction mixture. The remaining mixture of methyl pyranosides of 3,4-di-*O*-methyl-D-xylose yielded, by complete hydrolysis, a very satisfactory overall yield (66%) of the desired 3,4-di-*O*-methyl-D-xylopyranose. The identity of thus obtained *XII* with the product of the hydrolysis of *XI* was ascertained by the very close value of specific rotation of these two samples of 3,4-di-*O*-methyl-D-xylopyranose.

3,4-Di-*O*-methyl-D-xylopyranose is an appreciably volatile substance and could be further purified by vacuum distillation under relatively mild thermal conditions. This supports the previous assertion [17] that some erros in evaluating the results of methylation analysis may be attributed to the losses of certain methylated sugars during concentration of their solutions under vacuum.

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