

## Note

### Alternative syntheses of methylated sugars Part I. Methyl furanosides of 2-*O*-methyl- $\beta$ -xylose

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Identification and quantitative determination of the products of methanolysis of methylated polysaccharides is complicated by the fact that each sugar unit can yield up to four glycosides (two pyranosides and two furanosides). The formation of methyl pentofuranosides is usually more extensive than that of methyl hexofuranosides<sup>1-3</sup>. Authentic samples of methyl furanosides are generally prepared by methyl glycosidation of free sugars, followed by chromatography. This procedure is rather tedious and seldom<sup>4</sup> yields pure methyl furanosides in an appreciable quantity.

The present paper describes a more-convenient synthesis of methyl 2-*O*-methyl- $\alpha$ - and - $\beta$ -*D*-xylofuranosides which were hitherto unknown, although a mixture of the anomers had been obtained<sup>5</sup> as an intermediate in a synthesis of 2-*O*-methyl-*D*-xylose. Benzylation of 1,2-*O*-isopropylidene-*D*-xylofuranose and methanolysis of the product gave methyl 3,5-di-*O*-benzyl- $\alpha,\beta$ -*D*-xylofuranoside. Methylation of HO-2, followed by catalytic debenylation, gave methyl 2-*O*-methyl- $\alpha,\beta$ -*D*-xylofuranoside.

The  $\alpha,\beta$ -mixture of methyl 3,5-di-*O*-benzyl-2-*O*-methyl-*D*-xylofuranoside obtained by the above sequence was readily separable by chromatography on silica gel. Debenzylation of the isolated anomers with sodium in liquid ammonia<sup>6-8</sup> then gave methyl 2-*O*-methyl- $\alpha$ - and - $\beta$ -*D*-xylofuranoside. The  $\alpha$ -anomer crystallised readily, but the  $\beta$ -anomer could not be induced to crystallise and also gave syrupy di-*O*-benzoyl and di-*O*-acetyl derivatives\*.

#### EXPERIMENTAL

Melting points were determined on a Kofler hot-stage. Thin-layer chromatography (t.l.c.) was carried out on Silica gel G with (A) benzene-ethyl acetate (6:1), (B) chloroform-methanol (4:1), and (C) chloroform-acetone (10:1). Column chromatography was carried out on silica gel (0.15-0.25 mm) with (D) hexane-ethyl acetate (6:1) and (E) chloroform-acetone (9:2). On thin-layer plates, the components were located by spraying with 5% sulfuric acid in ethanol and heating. Solvents were removed under diminished pressure on a rotary evaporator at <40°.

*Methyl 3,5-di-O-benzyl-2-O-methyl- $\alpha$ - and - $\beta$ -D-xylofuranoside.* — Methyl

\*Note added in proof, see p. 493.

3,5-di-*O*-benzyl- $\alpha,\beta$ -D-xylofuranoside<sup>5</sup> (20 g) was dissolved in tetrahydrofuran (100 ml), and powdered sodium hydroxide (18 g) was added. With stirring, methyl sulphate (14 ml) was added dropwise, and the temperature was kept at 50° for 2 h, after which time t.l.c. (solvent *A*) showed complete disappearance of the starting material. Two spots ( $R_F$  0.32 and 0.43) were detected (*cf.* 0.15 and 0.27 for the starting material). The product was isolated, in the usual manner, as a yellow syrup (23 g, ~100%).

Elution of the  $\alpha,\beta$ -mixture from a column (100  $\times$  3.5 cm) of silica gel by using solvent *D* gave, as the faster-moving component, syrupy methyl 3,5-di-*O*-benzyl-2-*O*-methyl- $\beta$ -D-xylofuranoside (9.2 g, 46%),  $[\alpha]_D^{25} -45.8^\circ$  (*c* 1.1, ethanol).

*Anal.* Calc. for  $C_{21}H_{26}O_5$ : C, 70.4; H, 7.3;  $OCH_3$ , 17.3. Found: C, 70.4; H, 7.2;  $OCH_3$ , 18.2.

The slower-moving component was methyl 3,5-di-*O*-benzyl-2-*O*-methyl- $\alpha$ -D-xylofuranoside (7.3 g, 36.5%),  $[\alpha]_D^{25} +91.1^\circ$  (*c* 1.14, ethanol).

*Anal.* Calc. for  $C_{21}H_{26}O_5$ : C, 70.4; H, 7.3;  $OCH_3$ , 17.3. Found: C, 70.3; H, 7.2;  $OCH_3$ , 17.6.

An intermediate, mixed fraction (1.3 g) was also obtained.

*Methyl 2-O-methyl- $\alpha$ -D-xylofuranoside.* — A solution of methyl 3,5-di-*O*-benzyl-2-*O*-methyl- $\alpha$ -D-xylofuranoside (7 g) in 1,2-dimethoxyethane (10 ml) was added with stirring to liquid ammonia (100 ml), followed by addition of sodium (2 g) cut into small pieces. The last portion of sodium caused an intense blue colour to develop, which indicated that the reaction was complete. The syrupy product, isolated in the usual manner, was partitioned between chloroform and water, and the chloroform extract containing the main portion of bibenzyl (the reduction by-product) was discarded. T.l.c. (solvent *B*) of the aqueous solution showed one charring component ( $R_F$  0.45), and the solution was evaporated to dryness. The syrupy residue was chromatographed on a column (65  $\times$  2 cm) of silica gel with solvent *E*. Fractions containing the charring component were collected and evaporated to dryness, and the residue was crystallized from ether. Recrystallization from the same solvent did not raise the melting point (72–73°) of the title compound (3 g, 76.5%),  $[\alpha]_D^{25} +159^\circ$  (*c* 1.03, ethanol).

*Anal.* Calc. for  $C_7H_{14}O_5$ : C, 47.1; H, 7.92;  $OCH_3$ , 34.8. Found: C, 47.5; H, 7.87;  $OCH_3$ , 34.7.

*Methyl 2-O-methyl- $\beta$ -D-xylofuranoside.* — Methyl 3,5-di-*O*-benzyl-2-*O*-methyl- $\beta$ -D-xylofuranoside (5 g) was debenzylated, as described above, to give crude material as a pale-yellow syrup (2 g, 80.7%),  $R_F$  0.48 (solvent *B*). Distillation gave methyl 2-*O*-methyl- $\beta$ -D-xylofuranoside, b.p. 110° (bath)/0.1 mmHg,  $[\alpha]_D^{25} -83.5^\circ$  (*c* 1.30, ethanol) (Found: C, 47.1; H, 7.95;  $OCH_3$ , 34.7%). Neither the 3,5-diacetate nor the 3,5-dibenzoate could be obtained crystalline.

NOTE ADDED IN PROOF (Received November 2nd, 1970)

Methyl 2-*O*-methyl- $\beta$ -D-xylofuranoside gave crystalline (needles) di-*O*-*p*-nitrobenzoate, m.p. 91–93°,  $[\alpha]_D^{23} -87.1^\circ$  (*c* 1.07, acetone).

## REFERENCES

- 1 C. T. BISHOP AND F. P. COOPER, *Can. J. Chem.*, 40 (1962) 224.
- 2 C. T. BISHOP AND F. P. COOPER, *Can. J. Chem.*, 41 (1963) 2743.
- 3 V. SMERNYAGIN AND C. T. BISHOP, *Can. J. Chem.*, 46 (1968) 3085.
- 4 I. AUGESTAD AND E. BERNER, *Acta Chem. Scand.*, 8 (1954) 251.
- 5 W. D. S. BOWERING AND T. E. TIMELL, *Can. J. Chem.*, 36 (1958) 283.
- 6 A. J. BIRCH, *Quart. Rev. (London)*, 4 (1950) 69.
- 7 R. L. WHISTLER, T. J. LUTTENEGGER, AND R. M. ROWELL, *J. Org. Chem.*, 33 (1968) 396.
- 8 U. G. NAYAK AND R. L. WHISTLER, *J. Org. Chem.*, 34 (1969) 97.

*Carbohydr. Res.*, 16 (1971) 492-494