

At a composition  $ZrSn_{0.4}$ , the Guinier powder pattern photograph showed, in addition to the pattern of the defective  $Zr_3Sn_3$ , a number of strong, extra lines. Assuming a cubic unit cell, these extra lines could be indexed with  $a = 5.634 \text{ \AA}$ . The structure was found to be of the well-known  $\beta$ -wolfram structure type and should thus be given the formula  $Zr_3Sn$ .

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## Synthesis of Benzyl 4-O-Methyl- $\beta$ -D-Xylopyranoside

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Previous studies of a naturally occurring acetylated xylan<sup>1</sup> in birch wood have raised the question of whether the *O*-acetyl groups are attached to the most readily acetylated free hydroxyl groups in the  $\beta$ -1,4-linked anhydroxylose chains. In an attempt to investigate which of the two free hydroxyl groups at the 2- and 3-position is the most readily acetylated, benzyl 4-*O*-methyl- $\beta$ -D-xylopyranoside was selected as a suitable model for partial acetylation. The synthesis of this substance, by a sequence of reactions given below is analogous to that described by Hough and Jones<sup>2</sup> for the synthesis of the corresponding methyl glycoside, is reported in the present paper. The final product and all the intermediates were obtained in a crystalline form and the overall yield from D-arabinose was 10 % of the theoretical.

*Experimental.* All melting points are corrected. Evaporations were done under reduced pressure at a bath temperature below 40°.

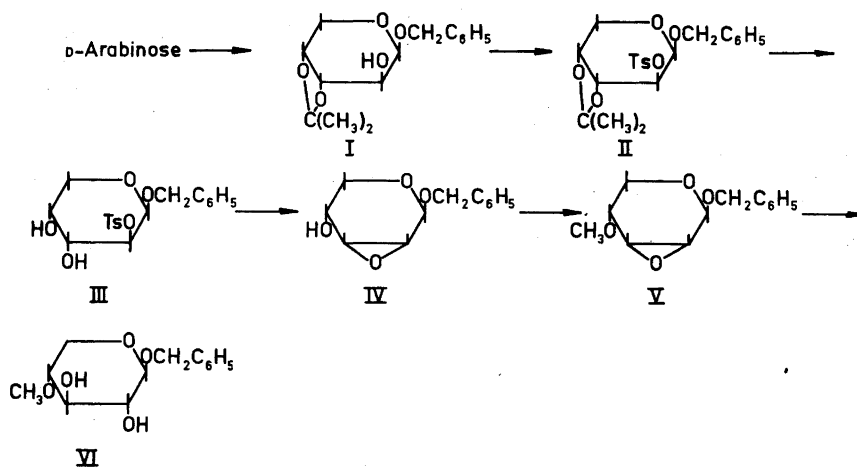
*Benzyl 3,4-isopropylidene-2-tosyl- $\beta$ -D-arabinopyranoside, II.* Benzyl-3,4-isopropyl-

idene- $\beta$ -D-arabinopyranoside (81 g, m. p. 55–57°,  $[\alpha]_D^{20} -195^\circ$ ), prepared from 100 g D-arabinose according to Ballou<sup>3</sup> was dissolved in pyridine (500 ml) and treated with *p*-toluenesulphonyl chloride (112 g). The solution was allowed to stand at room temperature during 48 h and then poured on ice. The mixture was extracted with chloroform and the chloroform solution was dried over anhydrous sodium sulphate, filtered and concentrated to dryness. The syrup obtained was used directly in the next step; a small quantity which was set aside crystallised from 96 % aqueous ethanol, m. p. 62–64° unchanged on further recrystallisation,  $[\alpha]_D^{20} -194^\circ$  (c 1.0 in chloroform). (Found: C 61.14; H 5.96; O 26.20; S 6.84. Calc. for  $C_{22}H_{26}O_7S$ : C 60.81, H 6.03; O 26.78; S 7.38.)

*Benzyl 2-tosyl- $\beta$ -D-arabinopyranoside, III.* The above product was dissolved in boiling acetone (900 ml) and 0.1 N formic acid (1 800 ml) was added over a period of 20 h under reflux. Concentration yielded a syrup which crystallised from aqueous ethanol. Recrystallisation from ethanol/isopropyl ether yielded benzyl 2-tosyl- $\beta$ -D-arabinopyranoside (70 g) with m. p. 120–123°. The pure substance had m. p. 123.5–124.5°,  $[\alpha]_D^{20} -156^\circ$  (c 0.8 in chloroform). (Found: C 57.40; H 5.52; O 27.94; S 7.88. Calc. for  $C_{19}H_{22}O_7S$ : C 57.86; H 5.62; O 28.39; S 8.13.)

*Benzyl 2,3-anhydro- $\beta$ -D-ribofuranoside, IV.* Benzyl 2-tosyl- $\beta$ -D-arabinopyranoside (70 g) was dissolved in methanolic sodium methoxide (1 l, made from 13 g sodium) and allowed to stand overnight. The solution was diluted with water (500 ml) and neutralised with sulphuric acid, the methanol was removed by vacuum distillation and the aqueous solution was extracted with chloroform. The combined chloroform solutions were dried over anhydrous sodium sulphate, filtered and the filtrate was concentrated to dryness. Spontaneous crystallisation occurred giving benzyl 2,3-anhydro- $\beta$ -D-ribofuranoside (29 g) with m. p. 64–76°. Recrystallisation from isopropyl ether gave 25 g with m. p. 74–76°. The pure substance had m. p. 76–77°,  $[\alpha]_D^{20} -67^\circ$  (c 0.8 in chloroform). (Found: C 64.60; H 6.13; O 29.04. Calc. for  $C_{12}H_{14}O_4$ : C 64.85; H 6.35; O 28.80.)

*Benzyl 4-O-methyl-2,3-anhydro- $\beta$ -D-ribofuranoside, V.* Benzyl 2,3-anhydro- $\beta$ -D-ribofuranoside (25 g) was methylated with methyl iodide (38 ml) and silver oxide



(30 g) in dimethyl formamide (500 ml) according to the method described by Kuhn *et al.*<sup>4</sup> and worked up as described by Bouveng<sup>5</sup>. The product crystallised spontaneously on concentrating a chloroform solution. Recrystallisation from ligroin yielded benzyl 4-*O*-methyl-2,3-anhydro- $\beta$ -D-xylopyranoside (23 g), m. p. 84–100° and a further recrystallisation yielded 21 g, m. p. 97–99°. The pure substance had m. p. 98–100°,  $[\alpha]_D^{20} -19^\circ$  (*c* 1.0 in chloroform). (Found: C 65.73; H 6.86; O 27.76. Calc. for  $C_{13}H_{16}O_4$ : C 66.08; H 6.83; O 27.09.)

*Benzyl 4-O-methyl- $\beta$ -D-xylopyranoside, VI.* Benzyl 4-*O*-methyl-2,3-anhydro- $\beta$ -D-xylopyranoside (21 g) was heated in 5% aqueous sodium hydroxide (1.5 l) in a boiling water bath for 60 h, cooled and neutralised with sulphuric acid. The aqueous solution was extracted exhaustively with chloroform, the combined chloroform solutions were dried over sodium sulphate, filtered and concentrated to dryness when spontaneous crystallisation occurred yield-

ing crude benzyl 4-*O*-methyl- $\beta$ -D-xylopyranoside (21 g) with m. p. 69–77°. Recrystallisation from *isopropyl* ether gave 17 g, m. p. 74–77°. The pure substance had m. p. 77.5–78°,  $[\alpha]_D^{20} -106^\circ$  (*c* 0.9 in chloroform). (Found: C 61.13; H 7.22; O 31.59. Calc. for  $C_{13}H_{18}O_5$ : C 61.40; H 7.13; O 31.46.)

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