177. *New Derivatives of Xylose.*

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IN view of the importance of xylose it is surprising that only a comparatively small number of its partially methylated derivatives have been prepared and characterised. Levene and Raymond (*J. Biol. Chem.*, 1933, **102**, 331) have characterised 3-methyl xylose and 5-methyl γ-xylose, and the preparation of 2-*methyl xylose*, 2 : 4-*dimethyl* β-*methylxyloside*, and 3 : 4-*dimethyl xylose* is now described. As 2 : 3-dimethyl xylose has already been obtained (Hampton, Haworth, and Hirst, J., 1929, 1739), of all the mono- and di-methyl derivatives of xylose which may be expected to exist, only 4-methyl xylose, 2 : 5-dimethyl γ-xylose, and 3 : 5-dimethyl γ-xylose (only known in the form of a lactone) remain to be prepared.

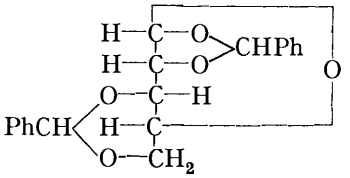
Convenient starting points were found in γ- and β-methylxyloside, both of which may be prepared in one operation by a suitable modification of the usual procedure for obtaining γ-methylxyloside.

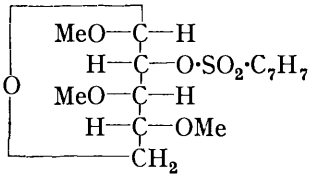
γ-Methylxyloside was condensed with acetone containing dry hydrogen chloride to give *monoacetone γ-methylxyloside*, a compound in which the acetone residue may be expected to be attached in positions 3 and 5 (compare Haworth and Porter, J., 1928, 611). Methylation with the Purdie reagents and subsequent hydrolysis with oxalic acid yielded a crystalline methyl xylose, which was proved to be 2-methyl xylose by the fact that it yielded xylosazone, with loss of a methyl group, on treatment with phenylhydrazine. Polarimetric observation of the new sugar during mutarotation showed that it possessed the β-configuration. It was farther characterised by the preparation of the following crystalline derivatives: 2-*methyl* β-*methylxyloside*, 3 : 4-*diacetyl* 2-*methyl* β-*methylxyloside*, and 3 : 4-*di*-p-*toluenesulphonyl* 2-*methyl* β-*methylxyloside*.

In a concurrent series of experiments, xylose readily condensed with benzaldehyde to yield a crystalline dibenzylidene xylose (compare van Ekenstein, *Rec. trav. chim.*, 1906, **25**, 153), but β-methylxyloside gave not the slightest trace of a benzylidene condensation compound. This behaviour is striking when compared with that of α-methylarabinoside, which readily yields 3 : 4-benzylidene α-methylarabinoside (Miss M. A. Ross, unpublished result). It follows that the *trans*-disposition of the hydroxyl groups on carbon atoms 3 and 4 in β-methylxyloside is unfavourable to the entry of a benzylidene residue in these positions, and it must be inferred that xylose reacts with benzaldehyde in the γ-form to give a dibenzylidene xylose of structure (I), which is analogous with that assigned to diacetone xylose by Haworth and Porter (*loc. cit.*). A partial hydrolysis of dibenzylidene xylose to a monobenzylidene derivative could not be effected.

3 : 5-Monoacetone γ-methylxyloside was converted into 3 : 5-*monoacetone* 2-*benzoyl γ-methylxyloside*, which, on treatment with methyl-alcoholic hydrogen chloride, gave 2-*benzoyl methylxyloside*. Methylation of this by means of the Purdie reagents did not appear to be accompanied by acyl rearrangement, but the reaction was complicated by a partial loss of the benzoyl group and it was necessary to provide for the elimination of fully methylated xylose which was formed through the exposure of the hydroxyl group in position 2. The resulting 2-*benzoyl* 3 : 4-*dimethyl methylxyloside* was submitted to alkaline and acid hydrolysis, after which 3 : 4-dimethyl xylose was isolated as a syrup. The sugar gave a dimethyl xylosazone on treatment with phenylhydrazine, from which it follows that position 2 is unsubstituted. On the other hand it failed to condense with methyl alcohol containing

hydrogen chloride at room temperature, from which it is inferred that position 4 is occupied. The structure assigned to the new sugar is therefore valid. 3 : 4-*Dimethyl* β-*methylxyloside* and 3 : 4-*dimethyl* 2-p-*toluenesulphonyl* β-*methylxyloside* (II) were prepared for purposes of characterisation.

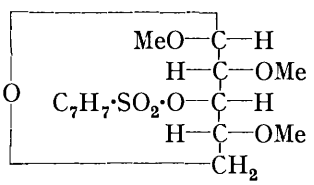
(I.) 



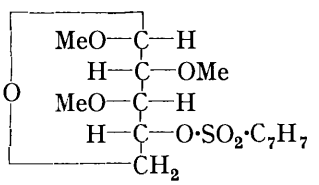
(II.)

M. p. 105°, $[\alpha]_D$ −34·8°.

β-Methylxyloside, condensed with triphenylchloromethane after the manner of Helferich (*Ber.*, 1925, **58**, 877), readily yielded a syrupy condensation product (compare Hudson and Hockett, *J. Amer. Chem. Soc.*, 1931, **53**, 4456). Acetylation of the syrup yielded a diacetyl derivative, and subsequent removal of the trityl residue a syrupy diacetyl β-methylxyloside, which, however, was readily converted into a crystalline diacetyl β-methylxyloside mononitrate. The nitrate group may be considered to have replaced the trityl group, as the experimental conditions throughout preclude the possibility of acyl rearrangement. The above crystalline derivative was converted into a new crystalline dimethyl β-methylxyloside, which yielded a crystalline *p*-toluenesulphonyl derivative (III). The constitution of the new sugar depends upon the position originally occupied by the trityl group, and direct diagnosis was difficult owing to lack of material. It was therefore decided to prepare 2 : 3-dimethyl xylose from xylan as described by Hampton, Haworth, and Hirst (*loc. cit.*), and to convert it into the corresponding β-methylxyloside for purposes of comparison. 2 : 3-*Dimethyl* β-*methylxyloside* was a syrup which, however, yielded crystalline 4-p-*toluenesulphonyl* 2 : 3-*dimethyl* β-*methylxyloside* (IV).

(III.) 

M. p. 88°, $[\alpha]_D$ −58·9°.



(IV.)

M. p. 56—59°, $[\alpha]_D$ −8·8°.

The structures ascribed to (II) and (IV) have been established; the only possible structure for the third isomeride, which was derived in the first place by condensing β-methylxyloside with triphenylchloromethane, is 3-p-*toluenesulphonyl* 2 : 4-*dimethyl* β-*methylxyloside* (III). It follows that the trityl residue enters the β-methylxyloside molecule in position 3, and that the derived substances are 2 : 4-*diacetyl* β-*methylxyloside* 3-*mononitrate* and 2 : 4-dimethyl β-methylxyloside.

Experimental.

The xylose used in this series of investigations was a much appreciated gift from the Department of Commerce, Bureau of Standards, Washington, and a supply of xylan was obtained through the courtesy of Messrs. Tullis, Russell and Co., Markinch.

Preparation of β- *and* γ-*Methylxyloside.*—A solution of xylose (30 g.) in methyl alcohol (750 c.c.) containing dry hydrogen chloride (12 g.) was kept at room temperature until it no longer reduced Fehling's solution (3—4 days). The product, isolated in the usual manner, was a viscous syrup (32 g.), which readily yielded a crystalline separation on treatment with acetone (25 c.c.); recrystallised once from absolute alcohol, pure β-methylxyloside, m. p. 156°, was obtained (yield, 8·5—11 g.). The acetone filtrate was evaporated to dryness under diminished pressure, and crude γ-methylxyloside obtained as a mobile syrup (yield, 20—22 g.).

3 : 5-*Monoacetone* γ-*Methylxyloside.*—A solution of γ-methylxyloside (20 g.) in acetone (250 c.c.) containing dry hydrogen chloride (2 g.) was kept at room temperature for 10 minutes and then neutralised by pouring into a dilute solution of potassium bicarbonate. The aqueous mixture was repeatedly extracted with chloroform; the united extracts were dried (sodium sulphate).

the solvent removed under diminished pressure, and the residue (8·7 g.) distilled in a vacuum, yielding **3** : 5-*monoacetone* γ-*methylxyloside* (5·2 g.), b. p. 102—107° (bath temp.)/0·1 mm., $[\alpha]_D$ + 17·3° in chloroform (c = 4·39) (Found : OMe, 14·2. $C_9H_{16}O_5$ requires OMe, 15·2%). The low yield is in part due to the crude nature of the γ-methylxyloside obtained above.

3 : 5-*Monoacetone* 2-*methyl* γ-*methylxyloside*, prepared by methylating the above compound with methyl iodide and silver oxide, was obtained in theoretical yield as a colourless mobile syrup, b. p. 77°/0·07 mm., $[\alpha]_D$ + 24·6° in chloroform (c = 3·532), $n_D^{15°}$ 1·4500 (Found : OMe, 27·1. $C_{10}H_{18}O_5$ requires OMe, 28·4%).

2-*Methyl xylose* was prepared by the simultaneous hydrolysis of the acetone and the methylxylosidic group. A solution of **3** : 5-monoacetone 2-methyl γ-methylxyloside (13 g.) in *N*-oxalic acid (130 c.c.) was boiled until the rotation became constant, cooled, neutralised with calcium carbonate, filtered, and evaporated to dryness under diminished pressure. The powdered residue was repeatedly extracted with boiling absolute alcohol and the united extracts were filtered through charcoal and evaporated to small bulk; 2-methyl xylose separated in colourless needles (7·3 g.), m. p. 132—133°. The new sugar was soluble in hot methyl and ethyl alcohols, hot acetone, and hot benzene. It showed an initial $[\alpha]_D$ −23·9° in water (c = 3·626), which changed to $[\alpha]_D$ + 34·8° in 90 minutes and to a final value of $[\alpha]_D$ + 35·9° in 20 hours (Found : OMe, 18·3. $C_6H_{12}O_5$ requires OMe, 18·9%). On treatment with phenylhydrazine dissolved in acetic acid it yielded an osazone which contained no methoxyl group; m. p. 157—158°, and 159—160° when mixed with authentic xylosazone (m. p. 160—161°).

Triacetyl 2-*methyl xylose* was prepared by treating 2-methyl xylose (6·5 g.), dissolved in pyridine (50 c.c.), with acetic anhydride (15 c.c.) at room temperature for 12 hours. The product was a pale yellow syrup (8·5 g.) which crystallised slowly from aqueous alcohol. Recrystallisation from absolute alcohol gave a product, m. p. 95°, which, when viewed under the microscope, was seen to consist of a mixture of plates and needles, and was probably a mixture of the α- and the β-form. The crystals showed $[\alpha]_D$ −2·2° in chloroform (c = 2·27) (Found : OMe, 11·2. $C_{12}H_{18}O_8$ requires OMe, 10·7%).

Preparation of **3** : 4-*Diacetyl* 2-*Methyl* β-*Methylxyloside*.—Triacetyl 2-methyl xylose (7·8 g.) was converted into the corresponding β-methylxyloside by treatment with hydrogen bromide dissolved in glacial acetic acid, followed by treatment with methyl alcohol and silver carbonate (Fischer, *Ber.*, 1916, **49**, 584). The product (6·5 g.), crystallised from ether–light petroleum (b. p. 40—60°), gave **3** : 4-*diacetyl* 2-*methyl* β-*methylxyloside* in colourless needles, m. p. 78—79°, $[\alpha]_D$ −38·1° in chloroform (c = 4·02) (Found : OMe, 22·7. $C_{11}H_{18}O_7$ requires OMe, 23·7%).

2-*Methyl* β-*Methylxyloside*.—**3** : 4-Diacetyl 2-methyl β-methylxyloside (5 g.) was dissolved in acetone (10 c.c.) and after the addition of *N*/2-sodium hydroxide solution (80 c.c.) the mixture was boiled for 15 minutes. An excess of solid potassium carbonate was added to the cooled reaction mixture, which was then extracted repeatedly with chloroform. On removal of the chloroform the product (2·9 g.) solidified to a hard mass of crystals, which were recrystallised from dry ether containing a little absolute alcohol. 2-*Methyl* β-*methylxyloside* separated in plates, m. p. 111—112°, $[\alpha]_D$ −67·7° in chloroform (c = 1·37) (Found : OMe, 34·2. $C_7H_{14}O_5$ requires OMe, 34·8%).

2-Methyl β-methylxyloside was converted by treatment with *p*-toluenesulphonyl chloride in pyridine solution into **3** : 4-*di*-p-*toluenesulphonyl* 2-*methyl* β-*methylxyloside*, which crystallised readily from absolute alcohol in colourless prisms, m. p. 123°, $[\alpha]_D$ −16·0° in chloroform (c = 3·3) (Found : OMe, 13·0. $C_{21}H_{26}O_9S_2$ requires OMe, 12·75%).

Attempted Condensation of β-*Methylxyloside with Benzaldehyde*.—In experiments carried out by the methods of Irvine and Scott (J., 1913, **103**, 585) and of Freudenberg (*Ber.*, 1928, **61**, 1750) condensation did not take place. Xylose, on the other hand, when submitted to Freudenberg's reaction, readily yielded dibenzylidene xylose, m. p. 135—136°, $[\alpha]_D$ + 21·5° in chloroform (c = 3·40). Van Ekenstein (*loc. cit.*) gives m. p. 130° and $[\alpha]_D$ + 37·5° in methyl alcohol.

Attempted Partial Hydrolysis of Dibenzylidene Xylose.—A solution of dibenzylidene xylose (1 g.) in a mixture of acetone (45 c.c.), water (4 c.c.), and *N*-hydrochloric acid (1 c.c.) was boiled until a constant rotation was recorded, polarimetric observations being made at intervals of 15 minutes.

Time, mins.	α_D.	$[\alpha]_D$.	Time, mins.	α_D.	$[\alpha]_D$.
Initial	+1·76°	+88°	75	+1·02°	+51°
15	+1·66	+83	90	+0·95	+47·5
30	+1·42	+71	105	+0·79	+39·5
45	+1·22	+61	120	+0·79	+39·5
60	+1·02	+51			

In a subsequent experiment the hydrolysis was arrested after 60 minutes, but no trace of a monobenzylidene derivative was detected, the product being a mixture of xylose and unchanged dibenzylidene xylose.

3 : 4-*Dimethyl Xylose.*—3 : 5-Monoacetone γ-methylxyloside (2·7 g.) was dissolved in pyridine (6 c.c.), cooled to 0°, and benzoyl chloride (1·7 c.c.) added drop by drop with constant shaking. The resulting solution was kept for 12 hours at room temperature, and the product then isolated by solution of the mixture in benzene, washing with dilute acid, alkali and water, and subsequent evaporation of the benzene solution. 3 : 5-*Monoacetone* 2-*benzoyl* γ-*methylxyloside* was obtained in quantitative yield (4 g.) as a clear viscous syrup which showed a distinct tendency to crystallise on standing, but purification by crystallisation was not attempted, as it would inevitably have led to large losses of material owing to the presence of α- and β-forms (Found: OMe, 10·4. $C_{16}H_{20}O_6$ requires OMe, 10·1%).

The above compound (6 g.) was dissolved in methyl alcohol (150 c.c.) containing 1·0% of dry hydrogen chloride, and the solution boiled for 45 minutes, during which time an initial rotation of $\alpha_D + 2·79°$ changed to a constant value of $\alpha_D + 0·81°$. The smell of methyl benzoate indicated that the benzoyl group was partially removed. The hot solution was neutralised with lead carbonate, filtered through animal charcoal, and evaporated under diminished pressure. The residue was dissolved in acetone, again filtered through animal charcoal, and on removal of the solvent 2-*benzoyl methylxyloside* (3·6 g.) was obtained as a hard glass (Found: OMe, 13·0. $C_{13}H_{16}O_6$ requires OMe, 11·6%). The high methoxyl content was undoubtedly due to the presence of methyl benzoate (OMe, 22·8%).

2-Benzoyl methylxyloside (3·6 g.) was methylated three times with the Purdie reagents until the refractive index became constant at $n_D^{15°}$ 1·4890. The resulting syrup was dissolved in benzene, the benzene solution extracted repeatedly with water to remove trimethyl methylxyloside formed through the loss of the benzoyl group and consequent exposure of the hydroxyl group to methylation, and the benzene solution dried over anhydrous sodium sulphate and evaporated to dryness; 2-*benzoyl* 3 : 4-*dimethyl methylxyloside* was obtained as a mobile syrup (3 g.), $n_D^{15°}$ 1·4992 (Found: OMe, 31·2. $C_{15}H_{20}O_6$ requires OMe, 31·4%).

Debenzoylation was carried out by a method similar to that described by Zemplén (*Ber.*, 1929, **62**, 1613). 2-Benzoyl 3 : 4-dimethyl methylxyloside (2·7 g.) was dissolved in methyl alcohol, a solution of sodium (0·1 g.) in methyl alcohol added, and the mixture boiled for 1 minute. After dilution with water the solution was evaporated under diminished pressure until oily drops of methyl benzoate ceased to come over. An excess of potassium carbonate was added to the aqueous residue, which was then extracted repeatedly with chloroform, and the united extracts were dried and evaporated to dryness. The resulting syrup might contain unchanged material in addition to 3 : 4-dimethyl methylxyloside. It was therefore dissolved in benzene and the solution was repeatedly extracted with water; the water extracts, after addition of potassium carbonate, were in turn extracted with chloroform; the chloroform extract was dried and evaporated in a vacuum to give a pale yellow syrup (0·9 g.), which on distillation yielded 3 : 4-*dimethyl methylxyloside* as a colourless syrup, b. p. 110—115° (bath temp.)/0·2 mm., $n_D^{15°}$ 1·4520 (Found: OMe, 48·6. $C_8H_{16}O_5$ requires OMe, 48·4%). The residual benzene solution referred to above contained unchanged material (0·3 g.).

3 : 4-Dimethyl methylxyloside (7 g.) was boiled with 3% hydrochloric acid (140 c.c.) and the hydrolysis was controlled polarimetrically. The initial rotation $[\alpha]_D + 10°$ changed to a constant value $[\alpha]_D + 20·4°$ in 50 minutes. The hot solution was neutralised with barium carbonate, and after filtration, was extracted with chloroform to remove unhydrolysed material. Thereafter the aqueous solution was evaporated to dryness and the residue was extracted with boiling acetone. The acetone extract was decolorised and evaporated; the residue was dissolved in dry ether, filtered and evaporated to give 3 : 4-*dimethyl xylose* (5·4 g.) as a colourless viscous syrup, $n_D^{15°}$ 1·4690, $[\alpha]_D + 24·9°$, changing to a final value of $[\alpha]_D + 20·5°$ in 4 hours in water ($c = 2·164$), and $[\alpha]_D + 5·3°$ in chloroform ($c = 4·13$) (Found: OMe, 34·8. $C_7H_{14}O_5$ requires OMe, 34·8%).

Attempted Condensation of 3 : 4-*Dimethyl Xylose with Acid Methyl Alcohol.*—A solution of 3 : 4-dimethyl xylose (0·5406 g.) in methyl alcohol containing 1% of dry hydrogen chloride was kept at room temperature. Polarimetric readings were taken at intervals, but after 2½ days the rotation had scarcely altered (+ 22·2° to + 25·5°) and the solution reduced Fehling's solution as vigorously as in the beginning. After 3 days the acid was neutralised with barium carbonate and the filtered solution was evaporated to dryness. The residue was purified by extraction with acetone, filtration, and evaporation in a vacuum. The product was a viscous syrup (0·4 g.), $n_D^{15°}$ 1·4673 (Found: OMe, 33·4. Calc. for $C_7H_{14}O_5$: OMe, 34·8%). No condensation had taken place.

3 : 4-Dimethyl xylose, when treated with phenylhydrazine and acetic acid in the usual manner, yielded a syrup which was essentially a dimethyl xylosazone (Found : OMe, 13·4; N, 14·7. $C_{19}H_{24}O_3N_4$ requires OMe, 17·4; N, 15·7%).

Preparation of 3 : 4-*Dimethyl* β-*Methylxyloside.*—(a) 3 : 4-Dimethyl xylose (1 g.) was converted into the corresponding dibenzoate, which was a reddish mobile syrup (2 g.), n_D 1·5569.

(b) A benzene solution of the dibenzoate was treated with a 40% solution of hydrogen bromide in glacial acetic acid (6 c.c.) and ether (9 c.c.) (Fischer, *loc. cit.*), whereby the benzoyl group in position 1 was replaced by a bromine atom. The reaction was allowed to proceed in a sealed vessel at room temperature for 2 hours; the solution was quickly washed with water, with a concentrated solution of potassium bicarbonate, and was dried over anhydrous sodium sulphate. Success in this preparation depends largely on a short contact with water at this stage.

(c) The replacement of the bromine with methoxyl was achieved by treatment of the above solution with methyl alcohol (20 c.c.) and silver carbonate (10 g.) on a mechanical shaker for 5 hours. The product obtained after removal of the silver and evaporation consisted of a dark-coloured syrup, which sometimes reduced Fehling's solution slightly on warming. In such cases it was methylated once with the Purdie reagents; reduction then disappeared entirely. The yield in the present case was 1·4 g.

(d) Debenzoylation was carried out by the method of Zemplén described above, and the final product was distilled in a vacuum. The mobile syrup obtained (0·75 g.), b. p. 110—115° (bath temp.)/0·15 mm., readily crystallised in small needles from ether–light petroleum (b. p. 40—60°). 3 : 4-*Dimethyl* β-*methylxyloside*, m. p. 89—90°, showed $[\alpha]_D$ −82·2° in chloroform (c = 2·085) (Found : OMe, 47·8. $C_8H_{16}O_5$ requires OMe, 48·4%). The substance was converted in good yield into 2-p-*toluenesulphonyl* 3 : 4-*dimethyl* β-*methylxyloside*, which crystallised from ether–light petroleum (b. p. 40—60°) in small colourless prisms, m. p. 105°, $[\alpha]_D$ − 34·8° in chloroform (c = 1·59) (Found : OMe, 26·6. $C_{15}H_{22}O_7S$ requires OMe, 26·9%).

Attempted Condensation of 3 : 4-*Dimethyl Xylose with Acetone.*—3 : 4-Dimethyl xylose (1·6 g.) was dissolved in acetone (40 c.c.) containing 1·5% of dry hydrogen chloride and the solution was observed polarimetrically. The rotation changed from an initial value of $[\alpha]_D$ + 18·2° to a constant value of $[\alpha]_D$ + 33·2° in 2¼ hours. The solution was then poured into a slight excess of potassium bicarbonate solution and the mixture was extracted with chloroform. The chloroform extract yielded a mobile syrup (0·6 g.), and unchanged dimethyl xylose (0·9 g.) was recovered from the water. The mobile syrup distilled easily, b. p. 98—105° (bath temp.)/0·15 mm., did not reduce Fehling's solution, and showed $n_D^{15°}$ 1·4520. The substance was not farther examined, but the physical constants suggest the possibility of its being a dimethyl anhydroxylose, since analysis showed that it contained no acetone (Found : OMe, 35·7. $C_7H_{12}O_4$ requires OMe, 38·8%. $C_{10}H_{18}O_5$ requires OMe, 28·4%).

2 : 4-*Dimethyl* β-*Methylxyloside.*—β-Methylxyloside (3 g.) was condensed with triphenylchloromethane (5·25 g.) as described by Helferich (*loc. cit.*). The resulting 3-trityl β-methylxyloside was a syrup (7·0 g.), which was acetylated to give a diacetyl derivative (syrup, 8·0 g.), from which the trityl residue was removed, by treatment of a benzene solution with dry hydrogen chloride, to give 2 : 4-*diacetyl* β-*methylxyloside* (1·0 g.) as a yellow syrup (Found : OMe, 12·1; COMe, 36·5. $C_{10}H_{16}O_7$ requires OMe, 12·5; COMe, 34·7%).

2 : 4-Diacetyl β-methylxyloside (1·2 g.) was converted into 2 : 4-*diacetyl* β-*methylxyloside* 3-*nitrate* by treating a solution in chloroform with fuming nitric acid (Oldham, J., 1925, **127**, 2840). The product (1·3 g.) crystallised from alcohol as colourless needles, m. p. 120—121°, $[\alpha]_D$ − 57·4° in chloroform (c = 1·843) (Found : OMe, 10·3. $C_{10}H_{15}O_9N$ requires OMe, 10·6%).

The above crystalline compound was converted into 2 : 4-*dimethyl* β-*methylxyloside* by means of the following processes.

(a) The deacetylation of 2 : 4-diacetyl β-methylxyloside 3-nitrate proved to be extremely difficult, as the ordinary methods led to the simultaneous removal of the acetyl and nitrate groups, and modifications of Zemplén's method (*loc. cit.*) led only to partial deacetylation. In the end recourse was had to dimethylamine. A solution of the partially deacetylated material (3·4 g.) in 33% alcoholic dimethylamine (10 c.c.) was kept over-night at room temperature, the solvent evaporated, and the residue heated for 2 hours at 100° under diminished pressure to eliminate acetodimethylamide. The crude β-methylxyloside 3-nitrate (2·8 g.) was methylated with methyl iodide and silver oxide until the refractive index became constant. The product was dissolved in benzene and extracted with water to remove fully methylated material which might have been formed through partial loss of nitrate and subsequent methylation. The benzene solution after drying and evaporation gave crude 2 : 4-*dimethyl* β-*methylxyloside* 3-*nitrate* as a mobile syrup (2·4 g.), $n_D^{15°}$ 1·4545. Distillation in a high vacuum was not attempted, as de-

composition would inevitably have ensued (Found: OMe, 37·7. $C_8H_{15}O_7N$ requires OMe, 39·2%).

(b) 2 : 4-Dimethyl β-methylxyloside 3-nitrate (2·2 g.) was dissolved in water containing just sufficient alcohol to give a homogeneous system, and freshly prepared 5% sodium amalgam (80 g.) was added in 10 g. portions during 3½ hours. A few drops of acetic acid were added at intervals to prevent excessive alkalinity. The reaction mixture, which gave an almost negative test for nitrate with diphenylamine, was neutralised with acetic acid and, after the addition of an excess of solid potassium carbonate, was extracted with chloroform. The dried chloroform extract was evaporated and yielded a dark coloured syrup (1·7 g.). In order to remove traces of unchanged material, the syrup was dissolved in benzene, and the solution exhaustively extracted with water; the aqueous extracts, after the addition of an excess of solid potassium carbonate, were extracted with chloroform and the chloroform extract was again evaporated to dryness to give a mobile syrup (1·45 g.). Distillation in a vacuum gave 1·3 g. of a colourless mobile syrup, b. p. 100—105° (bath temp.)/0·06 mm., $n_D^{15°}$ 1·4535, which crystallised readily from dry ether–light petroleum (b. p. 40—60°); after one recrystallisation 2 : 4-*dimethyl* β-*methylxyloside* was obtained in long colourless needles, m. p. 60—61°, $[\alpha]_D$ — 82·4° in chloroform (c = 1·377) (Found: OMe, 48·0. $C_8H_{16}O_5$ requires OMe, 48·4%).

3-p-*Toluenesulphonyl* 2 : 4-*dimethyl* β-*methylxyloside*, prepared in the usual way, crystallised from light petroleum (b. p. 40—60°) in small colourless needles, m. p. 88°, $[\alpha]_D$ — 58·9° in chloroform (c = 1·0) (Found: OMe, 25·8. $C_{15}H_{22}O_7S$ requires OMe, 26·9%).

2 : 3-Dimethyl xylose was prepared from xylan, by the methods employed by Hampton, Haworth, and Hirst (*loc. cit.*), as a syrup, $n_D^{15°}$ 1·4723, $[\alpha]_D$ + 19°, changing to + 20·1° in chloroform (c = 1·40). It was converted into the corresponding β-methylxyloside by methods already described, and 2 : 3-*dimethyl* β-*methylxyloside* was obtained as a syrup, b. p. 90—95° (bath temp.)/0·03 mm., $n_D^{15°}$ 1·4540, $[\alpha]_D$ — 5·8° in chloroform (c = 2·20) (Found: OMe, 48·5. $C_8H_{16}O_5$ requires OMe, 48·4%).

4-p-*Toluenesulphonyl* 2 : 3-*dimethyl* β-*methylxyloside* crystallised from light petroleum (b. p. 40—60°) in colourless needles, m. p. 56—59°, $[\alpha]_D$ — 8·8° in chloroform (c = 2·50) (Found: OMe, 24·9. $C_{15}H_{22}O_7S$ requires OMe, 26·9%).

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