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SYNTHESIS OF 2-*C*-METHYL-D-LYXOSE AND 2-*C*-METHYL-D-XYLOSE*

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ABSTRACT

The reaction of methyl 3,5-*O*-isopropylidene-β-D-*threo*-pentofuranosid-2-ulose (**1**) with methylmagnesium iodide or methyl-lithium gave methyl 3,5-*O*-isopropylidene-2-*C*-methyl-β-D-lyxofuranoside (**3**). Compound **1** reacted with diazomethane to give a *spiro*-epoxide that was reduced to yield **5**, the C-2 epimer of **3**. On the other hand, the anomer (**2**) of **1** reacted with methylmagnesium iodide or methyl-lithium to give methyl 3,5-*O*-isopropylidene-2-*C*-methyl-α-D-xylo- (**6**) and -lyxo-furanoside, respectively. The reaction of **2** with diazomethane and reduction of the resulting epoxides gave the same branched-chain sugars. Acid hydrolysis of **3** and **6** gave 2-*C*-methyl-D-lyxose and 2-*C*-methyl-D-xylose (**14**), respectively. Compound **14** was transformed into the 1,2:4,5-di-*O*-isopropylidene derivative. Some stereochemical aspects of the reactions are discussed.

INTRODUCTION

Of the 2-*C*-methylpentoses, only those with the D-[2] and -L-*arabino*[3], and D-[4] and L-*ribo*[3,5] configurations have been reported. 2-*C*-Methyl-L-lyxonic and -L-xylonic acids and their corresponding 1,4-lactones have been reported[6], but not the related sugars. We now report syntheses of the latter sugars in the D series.

RESULTS AND DISCUSSION

The reaction of methyl 3,5-*O*-isopropylidene-β-D-*threo*-pentofuranosid-2-ulose[7] (**1**) with methylmagnesium iodide or methyl-lithium in ether gave methyl 3,5-*O*-isopropylidene-2-*C*-methyl-β-D-lyxofuranoside (**3**) in yields of 54.5 and 27%, respectively. The configuration at C-2 in **3** was established by partial hydrolysis, to give the methyl glycoside **10**, and subsequent reacetonation to yield the more stable[8] methyl 2,3-*O*-isopropylidene-2-*C*-methyl-β-D-lyxofuranoside (**11**). On the other hand, **1** reacted with diazomethane to give 65% of a *spiro*-epoxide (**4**) that was quantitatively reduced with lithium aluminium hydride to give methyl 3,5-*O*-iso-

*Branched-chain Sugars, Part III. For Part II, see ref. 1.
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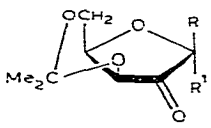
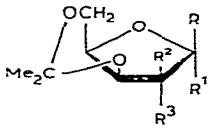
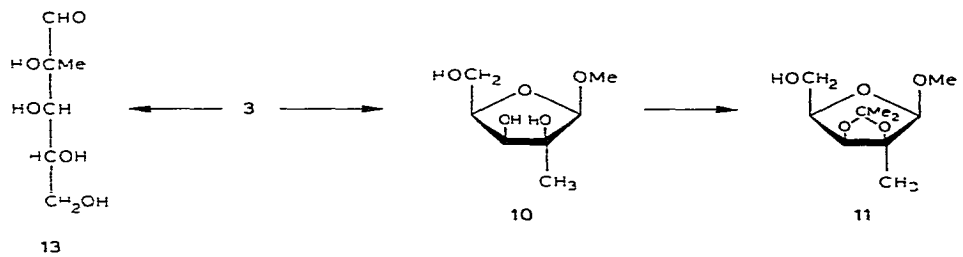
propylidene-2-*C*-methyl-β-D-xylofuranoside (**5**). That **5** was the C-2 epimer of **3** was shown by n.m.r. data. Thus, the ^1H spectrum of **3** showed singlets at δ 1.32, 1.39, 3.43, and 4.47, which were respectively assigned to Me-2, Me_2C, MeO-1, and H-1. The corresponding signals in **5** were at δ 1.35 (Me-2 and Me_2C), 3.37, and 4.67. These differences in chemical shift reflect the difference in configuration at C-2 in **3** and **5**.



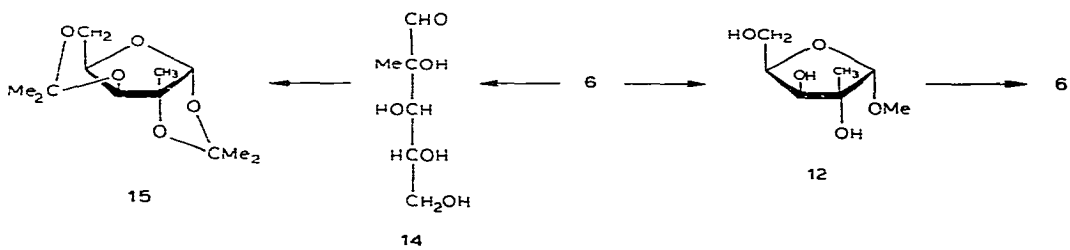
1 R = OMe, R^1 = H
2 R = H, R^1 = OMe



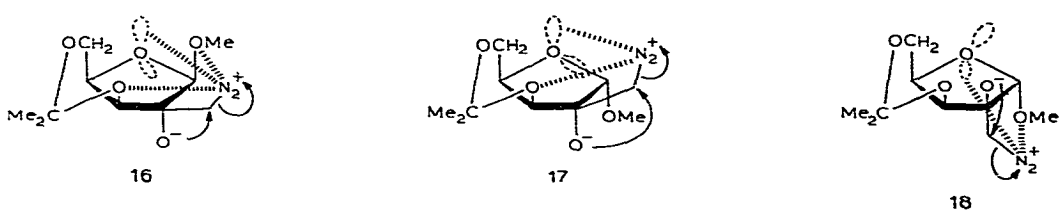
3 R = OMe, R^1 = H, R^2 = OH, R^3 = Me
4 R = OMe, R^1 = H, R^2 = $-CH_2-$, R^3 = $-O-$
5 R = OMe, R^1 = H, R^2 = Me, R^3 = OH
6 R = H, R^1 = OMe, R^2 = Me, R^3 = OH
7 R = H, R^1 = OMe, R^2 = OH, R^3 = Me
8 R = H, R^1 = OMe, R^2 = $-CH_2-$, R^3 = $-O-$
9 R = H, R^1 = OMe, R^2 = $-O-$, R^3 = $-CH_2-$



13 ← 3 → 10 → 11



15 ← 14 → 6 → 12 → 6



16 17 18

The reaction of the α anomer (**2**) of **1** with methylmagnesium iodide in ether gave 52.6% of methyl 3,5-*O*-isopropylidene-2-*C*-methyl-α-D-xylofuranoside (**6**), together with traces of the *lyxo* isomer **7**. That **6** had the D-*xylo* configuration was shown as follows. De-isopropylidenation of **6** gave 97.5% of the methyl glycoside **12**, re-acetonation of which produced **6**. In the same way, the reaction of **2** with methyllithium gave 56.9% of **7**, the C-2 epimer of **6**, as could be demonstrated by the n.m.r. data. The reaction of **2** with diazomethane yielded two *spiro*-epoxides (**8** and **9**) in yields of 28.3 and 50.4%, respectively. The configurations of **8** and **9** were established by reduction to the corresponding 2-*C*-methyl derivatives **6** and **7**.

The reaction of **1** with methylmagnesium iodide or methyl-lithium to give the D-*lyxo* product may be due to a preferential α attack of the nucleophile at the less-hindered side of the carbonyl group and also to the ability of magnesium to co-ordinate simultaneously with the carbonyl oxygen and vicinal oxygens[9]. In contrast, the β attack on **1** in the reaction with diazomethane may be explained by the hypothesis[10] that the diazomethyl cation in transition state **16** would be stabilised by O-1 and O-3 and also by the lone pair of electrons on the ring oxygen atom, giving the D-*xylo* product **4**.

Stereoselectivities of the reaction of **2** with methylmagnesium iodide or methyllithium are complementary and agree with those reported[3,5] for similar reactions of methyl 3,4-*O*-isopropylidene-β-L-*erythro*-pentopyranosid-2-ulose, where compounds have HO-2 *cis* and *trans*, respectively, to MeO-1. Similar results have been reported by Yoshimura *et al.*[11].

Low stereoselectivity in the reaction of **2** with diazomethane can be explained by the transition states **17** and **18**, leading to the *spiro*-epoxides **8** and **9**, where the diazomethyl cations would be stabilised by the vicinal oxygen atom and a lone pair of electrons; however, some steric effects could be involved, the β face being more hindered by the dioxolane ring than the α face, resulting in preferential attack at the α face and yielding **9** in higher yield.

Acid hydrolysis of **3** and **6** gave 2-*C*-methyl-D-lyxose (**13**) and 2-*C*-methyl-D-xylose (**14**), respectively. Compound **13** had a higher mobility in the presence of phenylboronic acid[12], reflecting the formation of a cyclic boronate with three hydroxyl groups in axial–equatorial–axial disposition in the $^1C_4$(β-D) conformation. Acetonation of **14** produced 82% of the di-*O*-isopropylidene derivative **15**.

The mass spectra of the new compounds described above agreed with those reported[13] for compounds of similar structure.

EXPERIMENTAL

General methods. — Melting points were determined with a Reichter hot-plate microscope, and are uncorrected. Solutions were dried over $MgSO_4$ before concentration under diminished pressure. ^{1}H-N.m.r. spectra (60 MHz, internal Me_4Si) were recorded with a Perkin–Elmer R-20B spectrometer, i.r. spectra with a Pye–Unicam SP1000 instrument, and mass spectra with a Hewlett-Packard 5930A Mass Spectro-

TABLE I

N.M.R. DATA (60 MHz, $CDCl_3$)

Compound	*Chemical shifts*[a] *(δ) (J in Hz)*											
	H-1	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5}$)	*H-5* ($J_{5,5'}$)	*H-5'* ($J_{4,5'}$)	*MeO*	*MeC-2*	*Me_2C*	*HO-2*	*HO-5*	*H-2'*[b] ($J_{2',2''}$)	*H-2''*[b]
3	4.47s		← 3.64–4.31 →			3.43s	1.32s	1.37s[c]	3.45s			
4	4.84s		← 3.92–4.41 →			3.47s		1.39s[c]			3.09d (4.50)	3.20d
5	4.67s (4.50)	3.85d (6.00)	4.30o (10.50)	3.96dd (10.5)	3.80dd	3.39s	1.35s	1.35s[c]	3.39s			
6	5.05s	4.11d (4.50)	4.36dd (2.25)	4.16d	4.16d (2.25)	3.70s	1.36s	1.50s[c]	3.20s			
7	4.87s		← 3.60–4.36 →			3.47s	1.34s	1.45s[c]	3.32s			
8	5.04s	4.07d (6.00)	4.20dd (3.00)	4.09d	4.09d (3.00)	3.43s		1.38s[c]			2.97d (6.00)	3.15d
9	5.13s		← 4.12s[d] →			3.44s		1.48s[c]			2.98d (6.00)	3.20d
11	4.42s	4.36d (4.50)	4.00m	← 3.92s →		3.52s	1.40s	1.48s 1.53s		2.70s[d]		
15	4.60s		← 3.87–4.24 →				← 1.37–1.55 →					

[a]Signal multiplicities: d, doublet; dd, double doublet; m, multiplet; o, octet; s, singlet. [b]Oxirane-ring protons at C-2. [c]Signal of two methyl groups. [d]Broad signal.

meter. Optical rotations were measured, unless otherwise stated, for solutions in chloroform (1-dm tube) with a Perkin–Elmer 141 polarimeter. G.l.c. was performed at 140° on a Carlo-Erba Model Fractovap G gas chromatograph equipped with a flame-ionisation detector and a glass column (2 m × 1.75 mm i.d.) packed with 3% of SE-52–LAC-741 (70:30) on Chromosorb G (100–120 mesh). The N_2 flow-rate was 30 mL/min, the injection-port temperature 170°, and the zone-detector temperature 160°. T.l.c. was performed on Silica Gel G (Merck), with detection by charring with sulfuric acid, using *A* ethyl acetate–hexane (1:1) and *B* ether–hexane (3:2). Column chromatography was performed on silica gel (Merck, 7734). Descending p.c. was performed on Whatman No. 1 paper with *C* 1-butanol–ethanol–water (28:7:13), and *D* 2% of phenylboronic acid in *C*; and detection with silver nitrate[14]. With solvent *D*, Brinton's method[15] was used prior to detection.

Reactions of methyl 3,5-O-isopropylidene-β-D-threo-pentofuranosid-2-ulose (**1**). — (*a*) *With methylmagnesium iodide.* To a stirred solution of methylmagnesium iodide (2 g, 12.5 mmol) in anhydrous ether (15 mL) was added, gradually, a solution of **1**[7] (742 mg, 3.7 mmol) in anhydrous ether (10 mL), and the mixture was heated under reflux. After 3 h, t.l.c. (solvent *A*) revealed that **1** had disappeared, and the presence of one product (R_F 0.40). The mixture was cooled, excess of methylmagnesium iodide was decomposed with 10% aqueous ammonium chloride, the organic layer was separated, and the aqueous layer was extracted with ether. Concentration of the combined organic layer and extracts gave a residue that was subjected to column chromatography (solvent *A*), to give **3** (436 mg, 54.5%), m.p. 46–47° (from hexane), $[\alpha]_D$ −86° (*c* 1.36), *T* 106 s, ν_{max}^{film} 3550 cm^{-1} (OH). Mass spectrum: *m/z* 203 (M^+ — Me), 187 (M^+ — MeO), 171, 143 (M^+ — Me — AcOH), 113 ($C_6H_9O_2^+$), 100 ($C_5H_8O_2^+$), 85 ($C_4H_5O_2^+$), and 43 (Ac^+). For ^{1}H-n.m.r. data, see Table I.

Anal. Calc. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 54.65; H, 8.58.

(*b*) *With methyl-lithium.* To a stirred suspension of small pieces of lithium (210 mg, 30 mmol) in anhydrous ether (5 mL) were added a few drops of methyl iodide. When reaction started, a solution of methyl iodide (2.13 g, 15 mmol) in anhydrous ether (10 mL) was added slowly to maintain gentle boiling. The mixture was stirred and heated until the lithium disappeared (1 h). After cooling, a solution of **1** (742 mg, 3.7 mmol) in anhydrous ether (15 mL) was added slowly with stirring, and the solution was stirred and heated under reflux for a further 2 h. T.l.c. (solvent *A*) showed that **1** had disappeared and that only **3** was present. The mixture was cooled and ether saturated with water and water were added with stirring until two layers were obtained. The aqueous phase was separated and extracted with ether (2 × 10 mL), and the combined ether solutions were washed with water (2 × 10 mL) and concentrated, to give a residue (346 mg) that was purified by column chromatography (solvent *A*) to yield **3** (217 mg, 27%).

(*c*) *With diazomethane.* To a solution of **1** (742 mg, 3.7 mmol) in methanol (20 mL) at 0° was added, portionwise, 2.8% ethereal diazomethane (10 mL) until the mixture remained yellow. The solution was stored for 2 days at room temperature. T.l.c. (solvent *A*) then revealed one product, R_F 0.65. Evaporation of the solvent gave

a residue (830 mg) which was subjected to column chromatography (solvent *A*), to give **4** (516 mg, 65.1%) as a syrup, *T* 156 s, $[\alpha]_D$ −61° (*c* 1.58). Mass spectrum: *m/z* 201 (M^+ — Me), 185 (M^+ — MeO), 173, 141 (M^+ — Me — AcOH), 113 ($C_6H_9O_2^+$), 85 ($C_4H_5O_2^+$), and 43 (Ac^+). For ^{1}H-n.m.r. data, see Table I.

Anal. Calc. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.21; H, 7.59.

Methyl 3,5-O-isopropylidene-2-C-methyl-β-D-xylofuranoside (**5**). — To a stirred solution of **4** (294 mg, 1.36 mmol) in anhydrous ether (15 mL) was added lithium aluminium hydride (100 mg), and the mixture was stirred and heated under reflux for 2 h. T.l.c. (solvent *A*) then showed that **4** had disappeared, and that one product (R_F 0.31) was present. The excess of hydride was decomposed by dropwise addition of ether saturated with water and 10% aqueous ammonium chloride. The ethereal layer was separated and the aqueous phase was extracted with ether (3 × 10 mL). The combined ether layer and extracts were concentrated to give a residue that was purified by column chromatography (solvent *A*), to yield **5** (298 mg, 98%), m.p. 59–60° (from hexane), $[\alpha]_D$ −102° (*c* 1.1), *T* 201 s, ν_{max}^{KBr} 3450 cm^{-1} (OH). Mass spectrum: *m/z* 203 (M^+ — Me), 187 (M^+ — MeO), 171, 145 (M^+ — Me — AcOH), 85 ($C_4H_8O_2^+$), and 43 (Ac^+). For ^{1}H-n.m.r. data, see Table I.

Anal. Calc. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.07; H, 8.46.

Reactions of methyl 3,5-O-isopropylidene-α-D-threo-pentofuranosid-2-ulose (**2**). — (*a*) *With methylmagnesium iodide*. To a stirred solution of methylmagnesium iodide (2 g, 12.5 mmol) in anhydrous ether (15 mL) was slowly added a solution of **2**[7] (1 g, 5 mmol) in the same solvent (10 mL). The mixture was stirred and heated under reflux. After 2 h, t.l.c. (solvent *B*) showed that **2** had disappeared and that one product (R_F 0.33) was present. The usual work-up of the reaction mixture gave a crystalline residue (700 mg). Recrystallisation from hexane yielded **6** (568 mg, 52.6%). T.l.c. of the mother liquors revealed **6** (*T* 118 s) and **7** (*T* 154 s). Compound **6** had m.p. 97–98°, $[\alpha]_D$ +86° (*c* 1.4), ν_{max}^{KBr} 3410 cm^{-1} (OH). Mass spectrum: *m/z* 218 (M^+), 203 (M^+ — Me), 187 (M^+ — MeO), 171, 143 (M^+ — Me — AcOH), 100 ($C_5H_8O_2^+$), 85 ($C_4H_5O_2^+$), and 43 (Ac^+). For ^{1}H-n.m.r. data, see Table I.

Anal. Calc. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 54.90; H, 8.40.

(*b*) *With methyl-lithium*. To a stirred solution of methyl-lithium (330 mg, 15 mmol) in anhydrous ether (10 mL) was slowly added a solution of **2** (1 g, 5 mmol) in anhydrous ether (15 mL). The mixture was stirred and heated under reflux for 2 h. T.l.c. (solvent *B*) then revealed that **2** had disappeared and that a new compound (R_F 0.35) had been formed. Treatment of the reaction mixture in the usual manner gave a syrupy residue which was purified by column chromatography (solvent *B*), to yield **7** (614 mg, 57%), m.p. 75–77° (from hexane), $[\alpha]_D$ +92° (*c* 1.17), *T* 154 s, ν_{max}^{KBr} 3500 cm^{-1} (OH). Mass spectrum: *m/z* 203 (M^+ — Me), 187 (M^+ — MeO), 171, 143 (M^+ — Me — AcOH), 100 ($C_5H_8O_2^+$), 85 ($C_4H_5O_2^+$), and 43 (Ac^+). For ^{1}H-n.m.r. data, see Table I.

Anal. Calc. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.58; H, 8.17.

(*c*) *With diazomethane*. To a solution of **2** (1 g, 5 mmol) in methanol (20 mL) at 0° was added, portionwise, 2.8% ethereal diazomethane (15 mL) until the mixture

remained yellow. The mixture was left for 2 days at room temperature. T.l.c. (solvent *B*) then showed two components, R_F 0.32 and 0.30. Evaporation of the solvent gave a residue (1 g) that was subjected to column chromatography (solvent *B*), to give, first, methyl 2,2[1]-anhydro-2-*C*-hydroxymethyl-3,5-*O*-isopropylidene-α-D-xylofuranoside (**8**; 303 mg, 28.3%), m.p. 86–87° (from hexane), $[\alpha]_D$ +179° (*c* 1.53), *T* 260 s. Mass spectrum: *m/z* 201 (M^+ — Me), 185 (M^+ — MeO), 173, 141 (M^+ — Me — AcOH), 113 ($C_6H_9O_2^+$), 111, 85 ($C_4H_5O_2^+$), and 43 (Ac^+). For ^{1}H-n.m.r. data, see Table I.

Anal. Calc. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.47; H, 7.40.

Reduction of **8** (283 mg, 1.3 mmol) with lithium aluminium hydride (100 mg) in anhydrous ether (15 mL) under reflux for 1 h gave **6** (272 mg, 95%).

Eluted second was methyl 2,2[1]-anhydro-2-*C*-hydroxymethyl-3,5-*O*-isopropylidene-α-D-lyxofuranoside (**9**; 539 mg, 50.4%), m.p. 116–118° (from hexane), $[\alpha]_D$ +180° (*c* 1.45), *T* 319 s. Mass spectrum: *m/z* 216 (M^+), 201 (M^+ — Me), 185 (M^+ — MeO), 173, 141 (M^+ — Me — AcOH), 113 ($C_6H_9O_2^+$), 111, 85 ($C_4H_5O_2^+$), and 43 (Ac^+). For ^{1}H-n.m.r. data, see Table I.

Anal. Calc. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.33; H, 7.58.

Reduction of **9** (187 mg, 0.86 mmol) with lithium aluminium hydride (100 mg) in anhydrous ether (15 mL) under reflux for 2 h gave **7** (168 mg, 89%).

Methyl 2,3-O-isopropylidene-2-C-methyl-β-D-lyxoside (**11**). — A solution of **3** (262 mg, 1.2 mmol) in methanol (30 mL) was stirred at room temperature with Amberlite IR-120 (H^+) resin (2 g) for 3 h. T.l.c. (solvent *A*) then showed that **3** had disappeared and that an immobile product was present (R_F 0.10, ethyl acetate). Filtration and evaporation of the solvent gave syrupy methyl 2-*C*-methyl-β-D-lyxoside (**10**; 213 mg, quantitative).

A solution of **10** (213 mg, 2.2 mmol) in dry acetone (10 mL) was stirred with powdered, anhydrous copper sulfate (1 g) and toluene-*p*-sulfonic acid (30 mg) for 1 day. T.l.c. (solvent *A*) then revealed that **10** had disappeared and that 2 products (R_F 0.19 and 0.40) were present. The mixture was neutralised with powdered, anhydrous potassium carbonate, filtered, and concentrated to give a residue (224 mg) that was subjected to column chromatography (solvent *A*), to yield **3** (18 mg, 7%) and **11** (190 mg, 73%) as a syrup, $[\alpha]_D$ −9.5° (*c* 1.37), *T* 236 s, ν_{max}^{film} 3500 cm^{-1} (OH). Mass spectrum: *m/z* 203 (M^+ — Me), 187 (M^+ — MeO), 185 (M^+ — Me — H_2O), 143 (M^+ — Me — AcOH), 127 (M^+ — MeO — AcOH), 125 (M^+ — Me — H_2O — AcOH), 85 ($C_4H_5O_2^+$), and 43 (Ac^+). For ^{1}H-n.m.r. data, see Table I.

Anal. Calc. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 54.69; H, 8.69.

Methyl 2-C-methyl-α-D-xylofuranoside (**12**). — Following the method described for **10**, **6** (157 mg, 0.72 mmol) was converted into **12** (125 mg, 97.5%), R_F 0.27 (ethyl acetate). This compound was acetonated, as described for **10**, to yield **6** (150 mg, 98.7%).

2-C-Methyl-D-lyxose (**13**). — A stirred suspension of **3** (391 mg, 1.8 mmol) in 0.5M sulfuric acid (10 mL) was heated at 100° until t.l.c. (ethyl acetate) showed that **3** had disappeared and that an immobile product was present. The mixture was

neutralised with Lewatid MP69 (HCO_3^-) resin, filtered, and concentrated to dryness, to give a syrup that was eluted from a column of microcrystalline cellulose (Merck) with 95% ethanol. The syrupy product **13** (193 mg, 64.3%) was homogeneous by p.c. [R_F 0.49 (solvent *C*), 0.71 (solvent *D*)] and had $[\alpha]_D$ −3° (*c* 1, water).

2-C-Methyl-D-xylose (**14**). — Hydrolysis of **6** (73 mg, 0.33 mmol), as described above, gave syrupy **14** (32 mg, 58.2%) that was homogeneous by p.c. [R_F 0.45 (solvent *C*)] and had $[\alpha]_D$ +1° (*c* 1.1, water).

1,2:3,5-Di-O-isopropylidene-2-C-methyl-α-D-xylofuranose (**15**). — A solution of **14** (80 mg, 0.5 mmol) in acetone (5 mL) was stirred with anhydrous copper sulfate (1 g) and toluene-*p*-sulfonic acid (30 mg) for 4 days. T.l.c. (solvent *B*) then revealed a compound (R_F 0.64). The mixture was neutralised with powdered, anhydrous potassium carbonate, filtered, and concentrated. Column chromatography (solvent *B*) of the semicrystalline mass gave **15** (100 mg, 86%), m.p. 132–134°, $[\alpha]_D$ +18° (*c* 1.1), *T* 168 s, ν_{max}^{KBr} 1385 and 1370 cm^{-1} (CMe_2). Mass spectrum: *m/z* 244 (M^+), 229 (M^+ — Me), 171 (M^+ — Me — Me_2CO), 169 (M^+ — Me — AcOH), 143 ($C_7H_{11}O_3^+$), 113 ($C_6H_9O_2^+$), 111 (M^+ — Me — Me_2CO — AcOH), 99, 83, 59 (Me_2COH^+), and 43 (Ac^+). For ^{1}H-n.m.r. data, see Table I.

Anal. Calc. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.20. Found: C, 59.02; H, 8.22.

REFERENCES

1 F. J. Lopez Aparicio, I. Izquierdo Cubero, and M. D. Portal Olea, *Carbohydr. Res.*, 103 (1982) 158–164.
2 J. J. K. Novak, *Collect. Czech. Chem. Commun.*, 39 (1974) 869–882.
3 J. S. Burton, W. G. Overend, and N. R. Williams, *J. Chem. Soc., C*, (1965) 3433–3455; R. J. Ferrier, W. G. Overend, G. A. Rafferty, H. M. Wall, and N. R. Williams, *ibid.*, (1968) 1091–1095.
4 A. A. Feast, B. Lindberg, and O. Theander, *Acta Chem. Scand.*, 19 (1965) 1127–1134.
5 A. A. Feast, W. G. Overend, and N. R. Williams, *J. Chem. Soc., C*, (1966) 303–306.
6 A. Ishizu, K. Yoshida, and N. Yamazaki, *Carbohydr. Res.*, 23 (1972) 23–29.
7 K. Bischofberger, A. J. Brink, O. G. de Villiers, R. H. Hall, and A. Jordan, *J. Chem. Soc., Perkin Trans. 1*, (1977) 1472–1476.
8 A. N. de Belder, *Adv. Carbohydr. Chem.*, 20 (1965) 219–302.
9 E. C. Ashby and J. J. Leammle, *Chem. Rev.*, 75 (1975) 521–546.
10 K.-I. Sato and J. Yoshimura, *Carbohydr. Res.*, 73 (1979) 75–84.
11 J. Yoshimura, Y. Ohgo, K. Ajisaka, and Y. Konda, *Bull. Chem. Soc. Jpn.*, 45 (1972) 916–921.
12 E. J. Bourne, E. M. Lees, and H. Weigel, *J. Chromatogr.*, 11 (1963) 253–257; R. J. Ferrier, W. G. Overend, G. A. Rafferty, H. M. Wall, and N. R. Williams, *Proc. Chem. Soc.*, (1963) 133.
13 D. C. DeJongh and K. Biemann, *J. Am. Chem. Soc.*, 86 (1964) 67–86.
14 W. E. Trevelyan, D. P. Procter, and J. S. Harrison, *Nature (London)*, 166 (1950) 444–445.
15 H. G. Britton, *Biochem. J.*, 73 (1959) 19.