SYNTHESIS OF A SERIES OF POSITIONALLY ISOMERIC METHYL O-(α- AND β-D-XYLOPYRANOSYL)-β-D-XYLOPYRANOSIDES*

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Crystalline α- and β-(1→2, 1→3 and 1→4)-linked methyl β-D-xylobiosides have been obtained by procedures based on condensation of 2,3,4-tri-O-acetyl-α-D-xylopyranosyl bromide with positionally isomeric methyl di-O-acetyl-β-D-xylopyranosides, followed by deacetylation. Per-O-acetates of the isomeric methyl β-D-xylobiosides were also obtained crystalline. The β-linked disaccharide methyl glycosides, methylated on a preparative scale, gave crystalline fully methylated products.

Xylans are the main type of noncellulosic polysaccharides of hardwoods.[1] Their main chain is known to be slightly branched[2,3]: some of the β-(1→4)-linked D-xylose units bear at $C_{(3)}$—OH D-xylopyranose or a short xylodextrin. Xylans branched at $C_{(2)}$—OH of D-xylose have also been described[4]. Due to the lack of conditions for selective chemical or enzymic depolymerisation only linear xylooligosaccharides have been isolated from the products of partial hydrolysis of this type of polysaccharides[5,6]. One of important structural features on which specific properties of polysaccharides depend is the mode of branching and, therefore, it is essential that model compounds representing the sites of branching be studied from various points of view. In the course of works aimed at the elaboration of methods of analysis of model reaction mixtures related to chemical processing of xylan-containing woods a need for reference substances arose. The present paper describes syntheses of a complete series of isomeric methyl β-D-xylobiosides *VII*, *VIII*, *XIII*, *XIV*, *XIX* and *XX*. The interglycosidic linkage such as in *VIII*, *XIV* and *XX* is typical for that occurring in natural xylans and the β-linked aglycon, protecting the reducing end-group of disaccharides, imitates the situation in the main backbone of the natural polymer.

Of the theoretically possible methyl β-D-xylobiosides only the β-(1→4)-linked compound has been described in the literature. Whistler and coworkers[7] obtained the substance by conversion of xylobiose isolated from products of partial hydrolysis of natural xylan, and the recently described chemical synthesis[8] of the same com-

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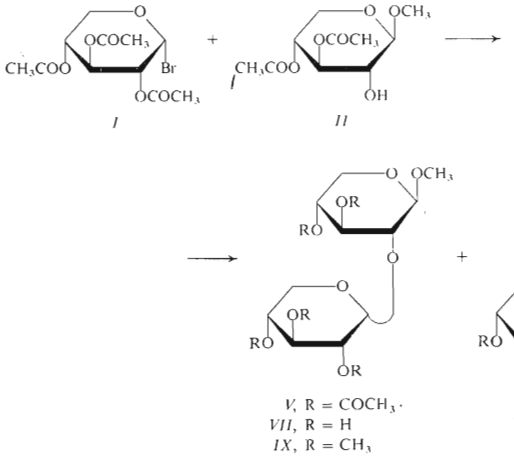
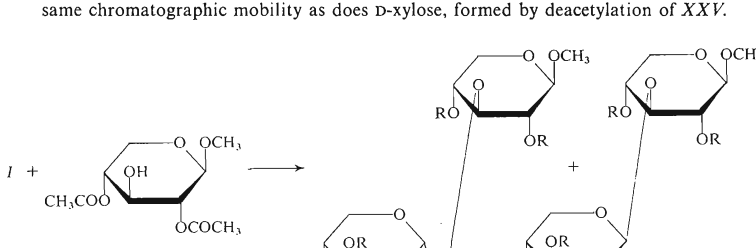
pound was based on alkaline hydrolysis of the product of condensation of 2,3,4-tri-O-acetyl-α-D-xylopyranosyl bromide[9] (*I*) with methyl 2,3-anhydro-β-D-ribopyranoside. The syntheses of isomeric methyl β-D-xylobiosides described below comprise condensations, under the conditions of modified Königs–Knorr synthesis, of *I* with positionally isomeric methyl di-O-acetyl-β-D-xylopyranosides[10–12] (*II–IV*), followed by deacetylation. In these reactions the condensation employing mercuric salts as catalysts and acid acceptors was preferred to those performed with silver salts, since it is known that the formers give higher yields. Also, possible migration of acetyl groups in partial acetates *II–IV*, previously observed[13] under the conditions of silver salt-catalyzed condensation of similar substrates, was excluded in this way.



The described preparative procedures resulted from a series of preliminary condensations of *I* with *II–IV* aimed at the optimalisation of the yields of the desired products. It has been found, that in order to drive the reaction of the starting diacetates to completion a considerable excess of bromide *I* has to be used and, in view of the crystallizing properties of the products, that the highest yields of the target products were obtained when the individual compounds were not isolated in the same manner. In looking for the most convenient working procedures partial hydrolysis of *I* during the condensation step (to give *XXV* having almost the same chromatographic mobility as *II–IV*) as well as the reaction of *I* with *XXV* (giving nonreducing disaccharides, *e.g. XXIII*) had to be taken into account. Since isomeric compounds

such as *XXIII* are in most cases chromatographically almost indistinguishable from the desired products, the presence of by-products made it difficult to estimate the composition of the reaction mixtures by TLC. More successful from this point of view was TLC of the deacetylated reaction mixtures. These always contained a variable amount of xylosyl xylosides (*e.g. XXIV*) and, when the condensation of *II*–*IV* was performed with a 100% molar excess of *I*, no methyl β-D-xylopyranoside, or only traces thereof, showing that *II*–*IV* had reacted virtually quantitatively. A real insight into the stereoselectivity of the condensation could not be gained in this way either since, unfortunately, some of the deacetylated methyl dipentosides show the same chromatographic mobility as does D-xylose, formed by deacetylation of *XXV*.

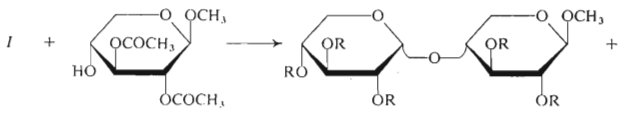


XI, R = $COCH_3$
XIII, R = H
XV, R = CH_3

XII, R = $COCH_3$
XIV, R = H
XVI, R = CH_3

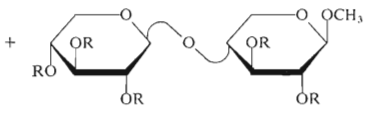
Isomeric methyl β-D-xylobiosides can be most conveniently isolated from the condensation products of *I* with *II*–*IV* in the manner described below. Methyl β-D-xylobiosides (1→2): Per-O-acetates *V* and *VI* can be obtained by fractional crystallisation of the crude product of condensation of *I* with *II*. Deacetylation of the individual compounds gives then glycosides *VII* and *VIII*. Further amounts of *VII* and *VIII* can be obtained by deacetylation of the material that remains after *V* and *VI* have been crystallized, and chromatography on a column of silica gel. During this operation compound *VII* is eluted together with some D-xylose which, however, does not interfere with the crystallisation of *VII*. Methyl β-D-xylobiosides (1→3): *a*) When the condensation of *I* with *III* is carried out in chloroform the per-O-acetate *XII* can be obtained from the crude product by crystallisation. Deacetylation of *XII* affords then the β-linked glycoside *XIV*. The α-interglycosidically linked substance *XIII*, together with a further crop of *XIV*, can be obtained by deacetylation of material that remains in the mother liquor after *XII* has been crystallized, and chromatography. Compounds *XIII* and *XIV* are well separable from each other and also

from D-xylose and xylosyl xylosides. *b*) When the condensation of *I* with *III* is performed in acetonitrile the crude product has to be chromatographed to afford pure *XIII* and *XIV* (the material that crystallizes from the crude product of condensation of *I* with *III* performed in acetonitrile melts unsharply at ~121–136°C; it is a mixture of *XII* and *XXII* in an approximate ratio of 4 : 1, as shown by TLC of the product of its deacetylation, revealing the presence of *XIV* and *XXIV*). Methyl

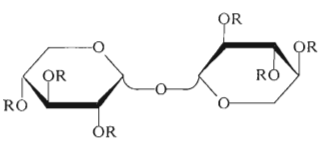


IV

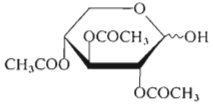
XVII, R = $COCH_3$
XIX, R = H
XXI, R = CH_3



XVIII, R = $COCH_3$
XX, R = H
XXII, R = CH_3



XXIII, R = $COCH_3$
XXIV, R = H



XXV

β-D-xylobiosides (1→4): The α-linked acetate *XVII* is obtained by chromatography on a column of silica gel of the crude product of condensation of *I* with *IV*; deacetylation of *XVII* then gives *XIX*. Eluted next from the column is the acetate *XVIII* together with *XXIII* and its isomers which all appear as one spot on TLC. Crystalline glycoside *XX* can be obtained by deacetylation of this mixture and chromatography,

the compound being well separated from *XXIV* and its isomers. Two crystalline modifications (m.p. 103–104 and 148·5–149°C) of methyl 4-O-(β-D-xylopyranosyl)-β-D-xylopyranoside have been described in the literature[7,8]. When an older (~2 years) sample of *XX*, originally melting sharply at 148·5–149°C, was thermoanalyzed[14] three endothermic peaks were recorded on the DTA curve, while no weight loss was observed, suggesting that the compound spontaneously recrystallized to its thermodynamically more stable forms. In the course of this work the hitherto unknown, highest melting modification of *XX* has been prepared.

Positionally isomeric β-linked methyl β-D-xylobiosides *VI*, *XII* and *XVIII* were methylated to give the fully methylated products *X*, *XVI* and *XXII*. Similarly, the α-linked methyl β-D-xylobiosides gave hexa-O-methyl derivatives *IX*, *XV* and *XXI*. The fact that the mass spectra of *IX* and *X*, *XV* and *XVI*, and *XXI* and *XXII* were qualitatively identical proved that the difference in the structure of these pairs of compounds is exclusively in the stereochemistry of the interglycosidic linkage. The physico-chemical constants of the prepared substances are summarized in Table I.

TABLE I
Physical Constants Found for the Synthesized Substances

Compound	M.p., °C	$[\alpha]_D$, °
V	159—160	+100·2
VI	142—143	— 62·2
VII	183—184	+ 70·2
VIII	153—154	— 71
X	66—67	— 83·3
XI	150—151	+ 45·5
XII	131—132	— 93
XIII	195—196	+ 87
XIV	161—162[a]	— 72
XVI	60—61	— 73·7
XVII	168—169[a]	+ 29·6
XVIII	145—146[b]	— 95
XIX	150—150·5	+ 57·5
XX	170—171[a,c]	— 74·8
XXII	87—88[a,d]	— 71·3

[a] The compound is polymorphous. [b] Lit.[7] m.p. 145—146°C, $[\alpha]_D$ —99·7°; lit.[8] m.p. 145·5 to 146·5°C, $[\alpha]_D$ —94°. [c] Lit.[7] m.p. 103—104°C, $[\alpha]_D$ —74·7°; lit.[8] m.p. 148·5—149°C, $[\alpha]_D$ —74·3°. [d] Lit.[7] m.p. 75·5—76°C, $[\alpha]_D$ —71°.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage. Optical rotations were measured with a Perkin–Elmer, Model 141 automatic polarimeter. Elemental analyses were determined using a Perkin–Elmer, Model 240 automatic C, H, N analyzer. The mass spectra (74 eV) were recorded at an emission of 100 μA with a JMS 100 D spectrometer. The temperature at the site of evaporation was 250°C and that of the ionizing chamber was 220°C. Thin-layer chromatography (TLC) on Silica Gel G was performed with: A benzene–acetone (6 : 1), and B chloroform–methanol (4 : 1). Preparative chromatography on dry-packed silica gel columns was done applying gradient elution with: C benzene–acetone (15 : 1)→(8 : 1), and D chloroform–methanol (8 : 1)→ →(5 : 1). Detection was carried out by *a*) charring with 5% sulphuric acid in ethanol, and *b*) by spraying with a solution of phthalic acid (1·66 g) and freshly distilled aniline (1 ml) in acetone (100 ml), and heating until permanent spots were visible. The detection *b*) revealed selectively substance *XXV* and D-xylose. Solutions in organic solvents were dried with anhydrous sodium sulphate and concentrated at 40°C/2 kPa.

Condensation of *I* with *II*

A mixture of *II* (2·5 g, 10 mmol)[10], drierite (5 g) and $Hg(CN)_2$ (2·5 g, 10 mmol) in acetonitrile (50 ml) was stirred with the exclusion of moisture for 1 h. Compound *I* (6·78 g, 20 mmol) was added, and after 1 h the mixture was diluted with chloroform and sodium hydrogen carbonate (2 g) was added. The mixture was stirred for further 10 min, filtered and the solids were washed with chloroform (3 . 50 ml). The combined filtrates were concentrated and the residue was partitioned between chloroform and 1M aqueous KBr solution. The chloroform solution was dried, concentrated and crystallisation from ethanol gave material (3 g) from which, after two recrystallisations from ethanol, 2·4 g (4·74 mmol) of methyl 3,4-di-O-acetyl-2-O-(2,3,4-tri-O--acetyl-β-D-xylopyranosyl)-β-D-xylopyranoside (*VI*), m.p. 142—143°C, $[\alpha]_D^{22}$ —62·2° (*c* 1, chloroform), was obtained. For $C_{21}H_{30}O_{14}$ (506·4) calculated: 49·80% C, 5·97% H; found: 49·60% C, 6·04% H.

The mother liquor was concentrated to a small volume and crystallisation from di-isopropyl ether gave 0·5 g of material which, after two recrystallisations from ethanol, afforded methyl 3,4-di-O-acetyl-2-O-(2,3,4-tri-O-acetyl-α-D-xylopyranosyl)-β-D-xylopyranoside (*V*, 0·3 g, 0·59 mmol), m.p. 159—160°C, $[\alpha]_D^{22}$ +100·2° (*c* 1, chloroform). For $C_{21}H_{30}O_{14}$ (506·4) calculated: 49·80% C, 5·97% H; found: 49·72% C, 6·01% H.

The mother liquor from which most of the acetates *V* and *VI* had been removed by crystallisation was worked-up as described later.

Compound *V* (0·25 g) was deacetylated as described for the preparation of *VIII* and the chromatographically pure product (R_F 0·20, solvent B, 130 mg, 90%) was crystallized from methanol–-acetone. Recrystallisation from the same solvent gave methyl 2-O-(α-D-xylopyranosyl)-β-D-xylopyranoside (*VII*), m.p. 183—184°C, $[\alpha]_D^{22}$ +70·2° (*c* 1, water). For $C_{11}H_{20}O_9$ (296·3) calculated: 44·59% C, 6·80% H; found: 44·70% C, 6·82% H.

A suspension of *VI* (1·5 g) in a mixture of methanol (75 ml) and methanolic 1M sodium methoxide (2 ml) was stirred at room temperature and with the exclusion of atmospheric moisture until all starting material dissolved (~1 h). After an additional 1 h TLC (solvent A and B) showed that the reaction was complete and that 1 product was formed (R_F 0·3, solvent B). The mixture was neutralized with Dowex 50 W (H^+-form) resin and, after filtration and concentration, the chromatographically homogeneous product (0·8 g, 91%) was crystallized from ethanol. After recrystallisation from ethanol and drying for 3 h at 100°C methyl 2-O-(β-D-xylopyranosyl)--β-D-xylopyranoside (*VIII*) showed m.p. 153—154°C and $[\alpha]_D^{22}$ —71° (*c* 1, water). For $C_{11}H_{20}O_9$ (296·3) calculated: 44·59% C, 6·80% H; found: 44·54% C, 6·82% H.

The material that remained in the mother liquor from which *V* and *VI* had been crystallized was deacetylated (Zemplén). TLC (solvent B) showed the presence mainly of substances having the same chromatographic mobility as *VII* (0·2) and *VIII* (R_F 0·3), and an authentic standard of α-D-xylopyranosyl β-D-xylopyranoside[15] (R_F 0·10). The presence of a small amount of D-xylose, poorly separated from *VII*, was revealed by the detection *b*). Chromatography on a column of silica gel gave 0·46 g (1·55 mmol) of chromatographically pure *VIII* (total yield of the isolated β-linked oligosaccharide, 2·4 g of *VI* isolated by crystallisation directly from the crude product of condensation of *I* with *II* +0·46 g of *VIII* obtained by chromatography of the deacetylated material in the mother liquor, 62·9%). Crystallisation from ethanol gave, after drying for 3 h at 100°C, *VIII* having m.p. 153—154°C. The α-linked isomer *VII* was eluted next, together with a small amount of D-xylose. Two recrystallisations from methanol–acetone or ethanol gave 0·35 g (1·18 mmol) of *VII* (total yield of the isolated α-linked oligosaccharide, 0·3 g of *V* isolated by fractional crystallisation from the crude product of condensation of *I* with *II* + 0·35 g of *VII* obtained by chromatography of the material in the deacetylated mother liquor, 17·7%), m.p. 183—184°C.

Sodium hydride (0·24 g) was added to a solution of compound *VIII* (190 mg) in N,N-dimethylformamide (6 ml) and the mixture was stirred with the exclusion of atmospheric moisture and carbon dioxide for 15 min. The mixture was cooled to 0°C and, after addition of methyl iodide (0·7 ml), stirring was continued at 20°C for 2 h. Water (10 ml) was added, the solution was neutralized (pH ~7·5) with 5% acetic acid, the product was extracted with chloroform, the chloroform solution was washed with water, dried and concentrated. TLC (solvent A) showed that only traces of undermethylated material were present (R_F <0·2) and the main component R_F 0·45) was isolated in a chromatographically pure state by elution of the crude product from a silica gel column with solvent C. The thus obtained methyl 3,4-di-O-methyl-2-O-(2,3,4-tri-O-methyl-β-D-xylopyranosyl)-β-D-xylopyranoside (*X*), 0·21 g (89%) had m.p. 66—67°C (from hexane, twice) and $[\alpha]_D^{22}$ —83·3° (*c* 1, chloroform). For $C_{16}H_{30}O_9$ (366·4) calculated: 52·44% C, 8·25% H; found: 52·66% C, 8·19% H.

The mass spectrum of compound *IX*, obtained by methylation of *VII* in the above-described manner, was qualitatively identical with that of *X*.

Condensation of *I* with *III*

a) A mixture of *III* (2·5 g, 10 mmol)[11], drierite (5 g), $Hg(CN)_2$ (2·5 g, 19 mmol) and $HgBr_2$ (0·5 g) in ethanol-free chloroform (50 ml) was stirred at room temperature and with the exclusion of atmospheric moisture for 1 h and, after the addition of bromide *I* (6·78 g, 20 mmol), the mixture was stirred for 18 h. The suspension was filtered, the filtrate washed with 1M aqueous KBr solution, then with water, dried and concentrated. Crystallisation from ethanol gave 2·4 g of material which, when recrystallized (twice) from the same solvent, afforded methyl 2,4-di-O-acetyl-3-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-β-D-xylopyranoside (*XII*, 2·05 g, 4·04 mmol) having m.p. 131—132°C and $[\alpha]_D^{22}$ —93° (*c* 1, chloroform). For $C_{21}H_{30}O_{14}$ (506·4) calculated: 49·80% C, 5·97% H; found: 49·84% C, 6·01% H.

Deacetylation of *XII* (1 g) as described for the preparation of *VIII* gave chromatographically pure (R_F 0·45, solvent B) methyl 3-O-(β-D-xylopyranosyl)-β-D-β-D-xylopyranoside (*XIV*, 0·54 g, 93 %). The substance, when crystallized from 2-propanol, melted almost completely at ~90°C, solidified on further heating at ~95°C and at 140—150°C recrystallized spontaneously into fibrous crystals that melted at 162—163°C. Recrystallisation from 1-propanol, after seeding with *XIV* which was previously heated to 160°C and allowed to come to room temperature, gave *XIV* melting sharply at 161—162°C and having $[\alpha]_D^{22}$ —72° (*c* 1, water). For $C_{11}H_{20}O_9$ (296·3) calculated: 44·59% C, 6·80% H; found: 44·63% C, 6·89% H.

The material that remained in the mother liquor after crystallisation of *XII* was deacetylated (Zemplén) and TLC (solvent B) showed that in addition to substances having the same chromatographic mobilities as *XIV* (R_F 0·45) and *XXIV* (R_F 0·10) traces of D-xylose (R_F 0·25) and another product (R_F 0·35), well separated from other components, were present. Chromatography on a column of silica gel with solvent D gave *XIV* (1·05 g, 3·54 mmol, combined yield of the β-linked disaccharide, 75·8%). Further eluted was methyl 3-O-(α-D-xylopyranosyl)-β-D-xylopyranoside (*XIII*, 0·45 g, 1·51 mmol, R_F 0·35, yield of the α-linked disaccharide, 15·1%), m.p. 195—196°C (from methanol, twice), $[\alpha]_D^{22}$ +87° (*c* 1, water). For $C_{11}H_{20}O_9$ (296·3) calculated: 44·59% C, 6·80% H; found: 44·52% C, 6·88% H.

Compound *XIII* (100 mg) in a mixture of pyridine (2 ml) and acetic anhydride (3 ml) was heated at 50°C until all the starting material dissolved, and the solution was left at room temperature for 18 h. The mixture was worked-up in the usual manner to give a chromatographically pure (solvent A) product (171 mg, ~100%). Crystallisation from ethanol (twice) yielded methyl 2,4-di-O-acetyl-3-O-(2,3,4-tri-O-acetyl-α-D-xylopyranosyl)-β-D-xylopyranoside (*XI*), m.p. 150 to 151°C, $[\alpha]_D^{22}$ +45·5° (*c* 1, chloroform). For $C_{21}H_{30}O_{14}$ (506·4) calculated: 49·80% C, 5·98% H; found: 50·07% C, 6·05% H.

b) Compounds *III* (2·5 g, 10 mmol) and *I* (6·78 g, 20 mmol) were allowed to react in acetonitrile (50 ml) with $Hg(CN)_2$ (2·5 g, 10 mmol) in the presence of drierite (5 g), the mixture was worked-up, and the crude product was deacetylated (Zemplén). TLC (solvent B) showed the presence of substances having the same chromatographic mobilities as *XIII*, *XIV*, D-xylose and *XXIV*. Chromatography on a column of silica gel afforded *XIV* as the fastest moving component (1·75 g, 59%) and 0·43 g (14·6%) of *XIII*. An intermediate, mixed fraction was also obtained.

Methylation of *XIV* (300 mg) in N,N-dimethylformamide (10 ml) with methyl iodide (1 ml) and sodium hydride (0·36 g) as described for the preparation of *X* gave, after purification of the crude product by column chromatography, pure methyl 2,4-di-O-methyl-3-O-(2,3,4-tri-O-methyl-β-D-xylopyranosyl)-β-D-xylopyranoside (*XVI*, 0·35 g, 94·3%). After crystallisation from hexane or pentane (twice) compound *XVI* melted at 60—61°C and had $[\alpha]_D^{22}$ —73·7° (*c* 1, chloroform). For $C_{16}H_{30}O_9$ (366·4) calculated: 52·44% C, 8·25% H; found: 52·57% C, 8·01% H.

Condensation of *I* with *IV*

Compounds *IV* (2·5 g, 10 mmol)[12] and *I* (6·78 g, 20 mmol) in acetonitrile (50 ml) were allowed to react with $Hg(CN)_2$ (2·5 g, 10 mmol) in the presence of drierite (5 g) as described for the preparation of *VI*. The crude product contained, as showed by TLC (solvent A), one main (R_F 0·4) and two minor products (R_F 0·5 and 0·3). The product having R_F 0·4 was chromatographically indistinguishable from authentic standards[8,15] of methyl 2,3-di-O-acetyl-4-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-β-D-xylopyranoside (*XVIII*) and α-D-xylopyranosyl β-D-xylopyranoside hexa-O-acetate (*XXIII*). The product having R_F 0·3 was indistinguishable according to TLC from 2,3,4-tri-O-acetyl-D-xylopyranose[15] (*XXV*). The mixture was chromatographed and the first eluted, sharply separated methyl 2,3-di-O-acetyl-(2,3,4-tri-O-acetyl-α-D-xylopyranosyl)-β-D-xylopyranoside (*XVII*, R_F 0·5, 1·32 g, 2·60 mmol, yield of the α-linked disaccharide, 26%) crystallized on concentration. Recrystallisation from methanol gave material that showed a double melting point which did not change on recrystallisation. A portion of uniform crystals melted at 150—155°C and the rest at 168—169°C, $[\alpha]_D^{22}$ +29·6° (*c* 1, chloroform). For $C_{21}H_{30}O_{14}$ (506·4) calculated: 49·80% C, 5·98% H; found: 49·67% C, 5·84% H.

The next eluted fraction (R_F 0·4) was deacetylated (Zemplén) and TLC (solvent B) showed that mainly methyl 4-O-(β-D-xylopyranosyl)-β-D-xylopyranoside (*XX*, R_F 0·25) and α-D-xylopyranosyl β-D-xylopyranoside (*XXIV*, R_F 0·1) were present, as shown by comparison with

authentic[8,15] standards. Elution from a column of silica gel gave *XX* (2·04 g, 6·89 mmol, yield of the β-linked disaccharide, 68·9%). Compound *XX* crystallized spontaneously from a concentrated ethanolic solution and melted at 148—149°C. When the trimorphous sample of *XX* (see above) was heated to 155° and allowed to come to room temperature the sample showed m.p. 168—170°C. When a dilute solution of *XX* in ethanol was seeded with a sample having m.p. 168—170° the material that crystallized showed m.p. 170—171°C and $[\alpha]_D^{22}$ —74·8° (*c* 1, water). For $C_{11}H_{20}O_9$ (296·3) calculated: 44·59% C, 6·80% H; found: 44·77% C, 6·80% H. Lit.[7] m.p. 103—104°C, $[\alpha]_D^{22}$ —74·7°; lit.[8] m.p. 148·5—149°C, $[\alpha]_D^{22}$ —74·3°.

Compound *XVII* (0·2 g) was deacetylated (Zemplén) and the chromatographically pure (R_F 0·25) methyl 4-O-(α-D-xylopyranosyl)-β-D-xylopyranoside (*XIX*, 0·11 g, 94%) crystallized when wetted with acetone. Recrystallisation from ethanol–acetone (twice) gave *XIX* melting at 150—150·5°C and having $[\alpha]_D^{22}$ +57·5° (*c* 1, water). For $C_{11}H_{20}O_9$ (296·3) calculated: 44·59% C, 6·80% H; found: 44·48% C, 6·77% H.

Compound *XX* (0·1 g) was treated with pyridine (0·5 ml) and acetic anhydride (1 ml) and the product, isolated in the usual manner, was crystallized from ethanol. Methyl 2,3-di-O-acetyl-4-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-β-D-xylopyranoside (*XVIII*), obtained in a virtually quantitative yield, showed m.p. 145—146°C and $[\alpha]_D^{22}$ —95° (*c* 1·5, chloroform). Lit[7,8] m.p. 145—146°C and $[\alpha]_D^{22}$ —94 to —99·7°.

Methylation of *XX* (0·2 g) in the manner described for the preparation of *X* gave, after purification of the crude product by column chromatography with solvent D, methyl 2,3-di-O-methyl-4-O-(2,3,4-tri-O-methyl-β-D-xylopyranosyl)-β-D-xylopyranoside (*XXII*, 0·22 g, 89%). After two crystallisations from hexane compound *XXII* showed m.p. 87—88°C and $[\alpha]_D^{22}$ —71·3° (*c* 1·8, chloroform). For $C_{16}H_{30}O_9$ (366·4) calculate: 52·44% C, 8·25% H; found: 52·28% C, 8·11% H. Compound *XXII* is obviously dimorphous: lit.[7] m.p. 75·5—76°, $[\alpha]_D^{22}$ —71°. Methylation of *XIX* as described above gave the fully methylated substance *XXI*, the mass spectrum of which was qualitatively identical with that of *XXII*.

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