SYNTHESIS AND ^{13}C NMR SPECTRA OF DISACCHARIDES RELATED TO GLUCOXYLANS AND XYLOGLUCANS

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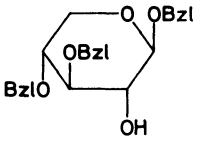
Received May 31, 1990
Accepted July 7, 1990

β-(1 → 2), (1 → 3) and (1 → 4) linked D-glucopyranosyl-D-xylopyranoses were obtained in high yields via condensation of 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide with the appropriate benzyl di-O-benzyl-β-D-xylopyranosides under conditions of modified Koenigs–Knorr reaction and deprotection of the acetyl and benzyl groups. 4-O-β-D-Xylopyranosyl-D-glucopyranose was synthesized similarly starting from 2,3,4-tri-O-acetyl-α-D-xylopyranosyl bromide and 1,2,3,6-tetra-O-acetyl-β-D-glucopyranose; it served as a xyloglucan model substance. The ^{13}C NMR spectra of final disaccharides and their intermediates are presented.

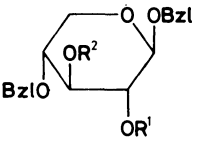
Synthetic oligosaccharides embodying xylose and glucose units are important particularly as model substances for structural analysis of less frequented plant polysaccharides, isolated e.g. from roots of ash-tree[1,2] (*Acer saccharum* MARSH), leaves of common barbery[3] (*Berberis vulgaris*) and eventually from other organic natural substances having variously binded saccharides (e.g. diterpenes – Baiyounoside[4]) in their molecules. No less important are these compounds as model substances for various biochemical studies (e.g. when testing cellulose and xylan degrading enzymes of *Aspergillus terreus*[5]).

This paper describes the preparation of three isomeric β-(1 → 2), (1 → 3) and (1 → 4) linked disaccharides related to glucoxylans *III*, *VIII*, *XIV* and one β-(1 → 4) linked disaccharide *XVII* related to xyloglucan. The β-(1 → 2) linked disaccharide *II* was synthesized by the Helferich's modification[6] of Koenigs–Knorr condensation employing acetonitrile as solvent and mercury dicyanide as catalyst and hydrogen bromide scavenger. Condensation of the hydroxy derivative[7] *I* with 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide[8] afforded compound *II* in crystalline form and in high yield (85%) applying the above-mentioned conditions. Deacetylation and atalytic hydrogenolysis deposited the already known 2-O-β-D-glucopyranosyl-D-xylopyranose (*III*), prepared in a substantially lower yield from methyl 3,5-O-isopropylidene-α,β-D-xyloside[8].

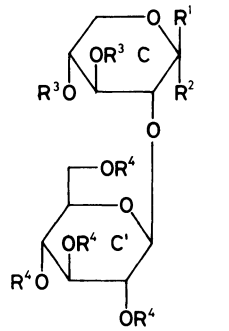
Synthesis of β-(1 → 3) linked disaccharide *VII* required a suitable starting derivative with a free OH group at C-3. To met this requirement benzyl 2,3-anhydro-4-O--benzyl-β-D-ribopyranoside[7] was treated with sodium allyloxide to yield the intermediate *IV* with the opened anhydro ring; benzylation of the latter furnished com-



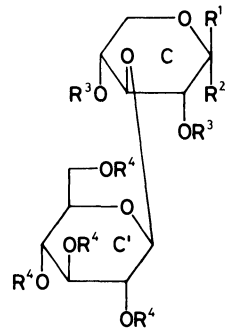
I



	R^1	R^2
IV	H	All
V	Bzl	All
VI	Bzl	H



	R^1	R^2	R^3	R^4
II	OBzl	H	Bzl	Ac
III	H, OH		H	H



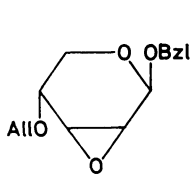
	R^1	R^2	R^3	R^4
VII	OBzl	H	Bzl	Ac
VIII	H, OH		H	H

Ac = acetyl , All = allyl , Bzl = benzyl

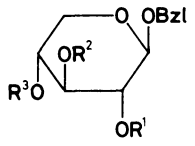
pound *V*, which was deallylated by palladium dichloride[9] to give benzyl 2,4-di-O--benzyl-β-D-xylopyranoside (*VI*) in 70% yield. Its condensation with 2,3,4,6-tetra-O--acetyl-α-D-glucopyranosyl bromide led to the substituted disaccharide *VII* in a 84% yield. Removal of protecting groups, similarly as with preparation of compound *III*, gave 3-O-β-D-glucopyranosyl-D-xylopyranose (*VIII*) obtained for the first time through a synthetic route. So far, it has been isolated as a product of β-glucosidase action on cellobiose and xylose[10–12].

To prepare the hydroxy derivative, required for the synthesis of the last of the isomeric disaccharides related to glucoxylans – compound *XIV* – benzyl 2,3-an-

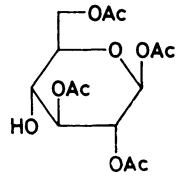
hydro-β-D-ribopyranoside[13] was allylated to the intermediate *IX*, the anhydro ring of which was opened by potassium hydroxide to 4-O-allyl-β-D-xylopyranoside (*X*). Its benzylation with benzyl bromide in N,N-dimethylformamide afforded *XI*, the deallylation of which furnished the crystalline benzyl 2,3-di-O-benzyl-β-D-xylopyranoside (*XII*). The latter reacted with 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide under catalysis of mercury dicyanide in dichloromethane to give the substituted disaccharide *XIII* isolated by means of column chromatography; removal of protecting groups deposited the crystalline, so far in literature not reported 4-O-β--D-xylopyranosyl-D-glucopyranose (*XIV*).



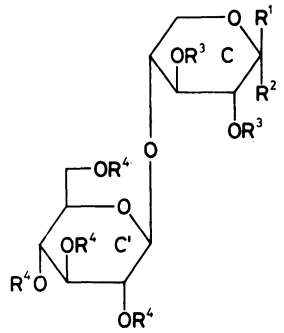
IX



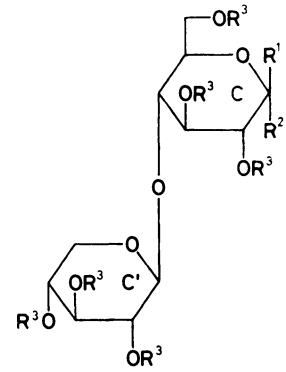
	R¹	R²	R³
X	H	H	All
XI	Bzl	Bzl	All
XII	Bzl	Bzl	H



XV



	R¹	R²	R³	R⁴
XIII	OBzl	H	Bzl	Ac
XIV	H, HO		H	H



	R¹	R²	R³
XVI	OAc	H	Ac
XVII	H, OH		H

The model disaccharide related to xyloglucans was synthesized from 1,2,3,6-tetra-O-acetyl-β-D-glucopyranose[14] (*XV*) on reaction with 2,3,4-tri-O-acetyl-α-D--xylopyranosyl bromide[15] in acetonitrile in the presence of mercury dicyanide. Deacetylation of the β-(1 → 4) linked peracetylated disaccharide *XVI* led to the desirable crystalline 4-O-β-D-xylopyranosyl-D-glucopyranose (*XVII*).

A 1·5–2-fold excess of the glycolysation reagent (acetobromoglucose or acetobromoxylose) was used in the preparation of all four condensations leading to

TABLE I

^{13}C NMR chemical shifts of skeletal carbons of mono- and disaccharides *II*–*XIV*, *XVI* and *XVII*

Compound	Ring	C-1	C-2	C-3	C-4	C-5	C-6
II	C	101·88	83·23	80·43	78·28	63·56	
	C′	100·42	72·15	73·27	68·25	71·84	61·95
III		93·19	81·96	73·05	70·62	61·87[a]	
	C_{β}^{α}	96·57	82·59	74·81	70·47	66·28	
		105·17	74·56	77·04	70·72	76·84	61·93[a]
	C'^{α}_{β}	104·03	73·05	77·35	70·89	77·04	62·08
IV	C	101·92	72·56	81·22	76·96	62·80	
V	C	103·12	81·67[a]	83·53[a]	77·71	63·98	
VI	C	102·74	81·21	77·34	75·70	63·96	
VII	C	102·75	81·46	82·24	75·86	64·13	
	C′	100·33	71·97	73·13	68·49	71·75	61·98
VIII	C_{β}^{α}	93·40	72·15	83·27	69·24	62·07	
		97·67	74·88	85·67	69·19	66·02	
	C'^{α}_{β}	104·05	74·73	77·27	70·90	76·85	62·01
		104·00	74·73	77·27	70·90	76·85	62·01
IX	C	94·52	52·15	50·24	69·30	59·51	
X	C	101·11	70·81[a]	70·89[a]	76·51	60·28	
XI	C	103·21	81·90[a]	83·76[a]	77·76	63·97	
XII	C	102·09	80·16	82·04	69·15	64·39	
XIII	C	103·21	81·40	82·09	78·31	63·23	
	C′	100·42	71·69	72·80	67·94	72·00	61·67
XIV	C_{β}^{α}	93·25	72·63[a]	72·31[a]	77·88	60·04	
		97·72	75·24	75·24	77·73	64·25	
	C′	102·37	74·12	76·80	70·83	77·20	61·97
XVI	C	91·61	71·34	73·42	76·79	73·03	62·24
	C′	101·49	70·43	71·08	68·74	61·72	
XVII	C_{β}^{α}	94·44	73·98	73·77	81·12	72·80	62·56
		98·36	76·64	77·43	80·97	76·75	62·68
	C′	105·86	75·75	78·26	71·80	67·79	

[a] The assignment can be interchanged.

substituted saccharides *II*, *VII*, *XIII* and *XVI* in order to complete the reaction of hydroxy derivatives *I*, *VI*, *XII* and *XV* and to compensate losses due to by-reactions (formation of the product of hydrolysis of the bromide and possibility to produce the disaccharide related to trehalose). Only the β-linked substituted disaccharides in question were chromatographically isolated from all reaction mixtures of the afore-mentioned condensations; other by-products present in small amounts (α-linked disaccharides, hydrolysis product of the bromine etc.) were neither isolated, nor studied.

The synthesized substituted (*II*, *VII*, *XIII* and *XVI*) or free (*III*, *VIII*, *XIV* and *XVII*) disaccharides, the hitherto unknown starting materials and their precursors (*IV*–*VI*, *IX*–*XII*) were characterized by basic physical constants and their structures were verified by the analysis of ^{13}C NMR spectra (Table I). The chemical shift data were ascribed according to already previously assigned signals in like substances[16–22] and known effects of substituents of protecting agents used.

EXPERIMENTAL

The melting points were estimated on a Kofler micro hot-stage, optical rotations were measured with a Perkin–Elmer, Model 241, polarimeter at 23°C; solvent systems for thin-layer chromatography on silica gel G and preparative chromatography on silica gel 60 (both Merck, Darmstadt, Germany, — the latter was prior to packing conditioned with 40% of the chromatographic systems) were: heptane–acetone 2 : 1, (S_1), 5 : 1 (S_2), tetrachloromethane–acetone 8 : 1 (S_3), 12 : 1 (S_4), tetrachloromethane–ethyl acetate 18 : 1 (S_5), benzene–acetone 5 : 1 (S_6), 10 : 1 (S_7), 15 : 1 (S_8). The spots were visualized by spraying with 5%-sulfuric acid in ethanol and heating to their constant intensity. The ^{13}C NMR spectra in deuteriochloroform solutions containing tetramethylsilane as an internal standard (compounds *II*, *IV*–*VII*, *IX*–*XIII* and *XVI*) or in D_2O solutions containing methanol as internal reference (δ 50·15 ppm) were recorded with Bruker AM-300 and Varian XL-200 spectrometers operating at 75 MHz and 50·3 MHz, respectively. The chemical shift values accurate to ±0·02 ppm are given on the δ scale. Acetonitrile was dried over calcium hydride, and distilled, dichloromethane was dried with phosphorus pentoxide and distilled. Solutions of products were dried with sodium sulfate and the solvents were removed at 40°C and 2 kPa.

Benzyl 3,4-di-O-Benzyl-2-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-β-D-xylopyranoside (*II*)

Consecutively mercury dicyanide (1·8 g, 7·1 mmol) and 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide[8] (2·9 g, 8·3 mmol) were added to the stirred solution of benzyl-3,4-di-O-benzyl-β-D-xylopyranoside[7] (*I*; 2·0 g, 4·8 mmol) in acetonitrile (20 ml) at 40°C for 1 h (till the absence of compound *I*, as monitored by thin-layer chromatography in S_1). The mixture was concentrated, dissolved in chloroform and extracted with 1M potassium bromide, the extract was washed with water, dried, concentrated and separated chromatographically using $S_3 \rightarrow S_4$. The disaccharide *II* (3·05 g, 85%) was crystallized from ethanol, m.p. 89·5–90·5°C, $[\alpha]_D$ −39·9° (*c* 1·0, chloroform). For $C_{40}H_{46}O_{14}$ (750·8) calculated: 63·99% C, 6·18% H; found: 64·16% C, 6·28% H.

2-O-β-D-Glucopyranosyl-D-xylopyranose (*III*)

The substituted disaccharide *II* (2·0 g, 2·7 mmol) suspended in methanol (100 ml) was left to stand with 1M sodium methoxide (1 ml) at room temperature for 30 min when its presence in the mixture disappeared (thin-layer chromatography in S_1). The mixture was neutralized by addition of the ion exchanger Dowex 50 W (H^+), filtered, condensed and hydrogenolyzed in methanol (100 ml) in the presence of 5% Pd/C (0·15 g) for 12 h. The catalyst was filtered off, the solvent was evaporated and the product *III* (0·75 g, 90%) was crystallized from ethanol, m.p. 199 to 201°C, $[\alpha]_D$ +15·9° (1 min), +3·4° (60 min, equilibrium) (*c* 0·7, water); ref.[8]: m.p. 200–202°C, $[\alpha]_D$ 0° (equil.). For $C_{11}H_{20}O_{10}$ (312·3) calculated: 42·31% C, 6·45% H; found: 42·14% C, 6·60% H.

Benzyl 3-O-Allyl-4-O-benzyl-β-D-xylopyranoside (*IV*)

Sodium hydride (1·9 g, 79·1 mmol) was gradually added to allyl alcohol (80 ml) with stirring. Benzyl 2,3-anhydro-4-O-benzyl-β-D-ribopyranoside[7] (4·0 g, 12·8 mmol) was introduced into the clear solution of sodium allyloxide and stirring was continued at 70–75°C for 7 h, when thin-layer chromatography in S_2 showed no starting material. The mixture was neutralized (Dowex 50 W, H^+) and chromatographed to yield 3·8 g (81%) of compound *IV* crystallizing from diisopropyl ether. M.p. 45–47°C, $[\alpha]_D$ −56·6° (*c* 0·9, chloroform). For $C_{22}H_{26}O_5$ (370·4) calculated: 71·33% C, 7·07% H; found: 71·3% C, 7·06% H.

Benzyl 3-O-Allyl-2,4-di-O-benzyl-β-D-xylopyranoside (*V*)

Sodium hydride (1·15 g, 48·0 mmol) was introduced into a cooled solution of benzyl 3-O-allyl--4-O-benzyl-β-D-xylopyranoside (*IV*; 3·0 g, 8·1 mmol) in 1,2-dimethoxyethane (30 ml). Benzyl bromide (1·9 ml, 16·2 mmol) was added to the mixture stirred at ambient temperature; the work--up after 2 h of stirring, when all starting material *IV* was consumed (thin-layer chromatography in S_8), afforded compound *V* (3·5 g, 94%) as colourless sirup $[\alpha]_D$ −36·5° (*c* 1, chloroform). For $C_{29}H_{32}O_5$ (460·6) calculated: 75·62% C, 7·0% H; found: 75·41% C, 6·85% H.

Benzyl 2,4-di-O-Benzyl-β-D-xylopyranoside (*VI*)

A 10%-solution of palladium dichloride (0·6 g, 0·3 mmol $PdCl_2$), sodium acetate (0·6 g, 7·3 mmol), acetic acid (5·6 ml, 98 mmol) and water (0·3 ml, 16·7 mmol) were added to benzyl 3-O-allyl--2,4-di-O-benzyl-β-D-xylopyranoside (*V*; 1·4 g, 3·0 mmol) and the mixture was heated at 70°C for 24 h. Two more portions of 10%-$PdCl_2$ (0·3 g each) were added within further 24 h. After 48 h the mixture was filtered, concentrated, diluted with chloroform, neutralized with aquoues solution of sodium hydrogen carbonate, dried and the solvent was evaporated. The product *VI* was separated chromatographically with S_5 and crystallized from ethanol. Yield 0·9 g (70%), m.p. 72–73°C, $[\alpha]_D$ −23·7° (*c* 0·8, chloroform). For $C_{26}H_{28}O_5$ (420·5) calculated: 74·26% C, 6·71% H; found: 74·15% C, 6·87% H.

Benzyl 2,4-di-O-Benzyl-3-O-(2,3,4,6-tetra-O-acetyl-β-D--glucopyranosyl)-β-D-xylopyranoside (*VII*)

2,3,4,6-tetra-O-Acetyl-α-D-glucopyranosyl bromide[8] (1·5 g, 4·3 mmol) was added to benzyl--2,4-di-O-benzyl-β-D-xylopyranoside (*VI*; 1·0 g, 2·4 mmol) and mercury dicyanide (0·9 g, 3·6 mmol) in acetonitrile (10 ml). The mixture was stirred at 40°C for 2 h, till only traces of the starting material were detectable on thin-layer chromatography in S_1. The mixture was purified chromato-

graphically with S_2 to give the title product *VII* (1·5 g, 84%) as a colourless sirup, $[\alpha]_D$ −18° (*c* 1, chloroform). For $C_{40}H_{46}O_{14}$ (750·8) calculated: 63·99% C, 6·18% H; found: 64·2% C, 6·21% H.

3-O-β-D-Glucopyranosyl-D-xylopyranose (*VIII*)

The disaccharide *VII* (1·0 g, 1·53 mmol) was deacetylated and debenzylated using aliquot amounts of reagents and solvents and employing the procedure described with preparation of *III*. The yield of 3-O-β-D-glucopyranosyl-D-xylopyranose (*VIII*) was 0·39 g (94%), colourless sirup, $[\alpha]_D$ −8·2° (1 min), +10·6° (80 min, equilibrium) (*c* 1, water). For $C_{11}H_{20}O_{10}$ (312·3) calculated: 42·31% C, 6·45% H; found: 42·14% C, 6·32% H.

Benzyl 4-O-Allyl-2,3-anhydro-β-D-ribopyranoside (*IX*)

Sodium hydride (1·1 g, 45·8 mmol) was added at 0°C to benzyl 2,3-anhydro-β-D-ribopyranoside[13] (5·0 g, 22·6 mmol) in 1,2-dimethoxymethane (50 ml). Allyl bromide (2·9 ml, 34·3 mmol) was then introduced dropwise into the stirred mixture at room temperature. The starting material was consumed within 30 min (thin-layer chromatography in S_7); the mixture was then diluted with methanol (15 ml), neutralized with dilute acetic acid and concentrated. The product was exhaustively extracted with chloroform and crystallized from diisopropyl ether. Yield 4·9 g, (83%), m.p. 34—34·5°C, $[\alpha]_D$ −12·8° (*c* 1, chloroform). For $C_{15}H_{18}O_4$ (262·3) calculated: 68·68% C, 6·92% H; found: 68·89% C, 6·97% H.

Benzyl 4-O-Allyl-β-D-xylopyranoside (*X*)

Benzyl 4-O-allyl-2,3-anhydro-β-D-ribopyranoside (*IX*; 3·0 g, 11·5 mmol) was added to a freshly prepared 10%-aqueous potassium hydroxide (150 ml) and the mixture was stirred and refluxed for 12 h, when the starting compound *IX* was already totally consumed (thin-layer chromatography in S_6). The solution was then cooled, neutralized (Dowex 50 W, H^+), concentrated and chromatographically separated with S_7 to furnish *X* (2·8 g, 87%) (crystallized from diisopropyl ether), m.p. 50·5—51·5°C, $[\alpha]_D$ −105·3° (*c* 0·9, chloroform). For $C_{15}H_{20}O_5$ (280·3) calculated: 64·27% C, 7·19% H; found: 64·38% C, 7·15% H.

Benzyl 4-O-Allyl-2,3-di-O-benzyl-β-D-xylopyranoside (*XI*)

Sodium hydride (0·5 g, 20·8 mmol) was gradually added into a solution of compound *X* (2·0 g, 7·1 mmol) in N,N-dimethylformamide (20 ml) cooled to 0°C. Afterwards, benzyl bromide (1·9 ml, 16·0 mmol) was introduced and the mixture was stirred at room temperature for 1 h, when thin-layer chromatography in S_6 confirmed the absence of compound *X*. The work-up afforded substance *XI* (3·0 g, 91%), which crystallized from isopropyl alcohol. M.p. 64—65°C, $[\alpha]_D$ −13·6° (*c* 1, chloroform). For $C_{29}H_{32}O_5$ (460·6) calculated: 75·62% C, 7·0% H; found: 75·67% C, 7·03% H.

Benzyl 2,3-di-O-Benzyl-β-D-xylopyranoside (*XII*)

Compound *XI* (2·0 g, 4·3 mmol), palladium dichloride (10%-solution, 1·3 g, 0·7 mmol $PdCl_2$) and sodium acetate (0·85 g, 10·4 mmol) suspended in acetic acid (8 ml, 139·9 mmol) and water (0·4 ml, 22·2 mmol) were heated at 70°C for 40 h. The mixture was worked up as with the hydroxy derivative *VI* and crystallized from diisopropyl ether. Yield 1·5 g (82%), m.p. 123·5 to

125°C, $[\alpha]_D$ −54·3° (*c* 1, chloroform). For $C_{26}H_{28}O_5$ (420·5) calculated: 74·26% C, 6·71% H; found: 74·11% C, 6·82% H.

Benzyl 2,3-di-O-Benzyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D--glucopyranosyl)-β-D-xylopyranoside (*XIII*)

Molecular sieve 4 Å (0·3 g), mercury dicyanide (0·18 g, 0·71 mmol) and 2,3,4,6-tetra-O-acetyl-α--D-glucopyranosyl bromide[8] (0·25 g, 0·72 mmol) were added to compound *XII* (0·2 g, 0·5 mmol) in dichloromethane (2 ml) and stirred at room temperature for 24 h. During this time the starting material was consumed (thin-layer chromatography in S_1), the mixture was worked up and separated chromatographically with S_2 to deposit the disaccharide *XIII* (0·28 g, 78%), which crystallized from methanol; m.p. 128·5—130°C, $[\alpha]_D$ −30° (*c* 0·8, chloroform). For $C_{40}H_{46}O_{14}$ (750·8) calculated: 63·99% C, 6·18% H; found: 63·87% C, 6·28% H.

4-O-β-D-Glucopyranosyl-D-xylopyranose (*XIV*)

Deacetylation of compound *XIII* (0·25 g, 0·33 mmol) by 1M solution of sodium methoxide (0·15 ml) in methanol (15 ml) followed by hydrogenolysis in methanol (10 ml) in the presence of 5%-Pd/C (20 mg) and under the same conditions as described with *III* afforded the disaccharide *XIV* (85 mg, 85%) as a colourless sirup, $[\alpha]_D$ −3° (1 min), +4° (60 min, equilibrium) (*c* 0·5, water). For $C_{11}H_{20}O_{10}$ (312·3) calculated: 42·31% C, 6·45% H; found: 42·2% C, 6·56% H.

1,2,3,6-tetra-O-Acetyl-4-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-β-D-glucopyranose (*XVI*)

A freshly prepared 2,3,4-tri-O-acetyl-α-D-xylopyranosyl bromide[15] (2·0 g, 5·9 mmol) was added to a mixture consisting of 1,2,3,6-tetra-O-acetyl-β-D-glucopyranose[14] (*XV*; 1·0 g, 2·87 mmol) and mercury dicyanide (1·5 g, 5·9 mmol) in acetonitrile with stirring. After 2 h compound *XV* was consumed (thin-layer chromatography in S_1), the mixture was worked up and chromatographed with S_2 to afford the substituted disaccharide *XVI* (1·15 g, 66%), m.p. 160—161°C (ethanol), $[\alpha]_D$ −36·6° (*c* 0·9, chloroform). For $C_{25}H_{34}O_{17}$ (606·5) calculated: 49·50% C, 5·65% H; found: 49·49% C, 5·72% H.

4-O-β-D-Xylopyranosyl-D-glucopyranose (*XVII*)

Compound *XVI* (1·0 g, 1·6 mmol) was deacetylated with 1M sodium methoxide (0·5 ml) in methanol (50 ml) at room temperature. The product was neutralized with Dowex 50 W (H^+) after 2 h, when no starting material could be detected (thin-layer chromatography in S_8) and crystallized from methanol. Yield 0·5 g (97%), m.p. 218—220°C, $[\alpha]_D$ +24·5° (*c* 1, water). For $C_{11}H_{20}O_{10}$ (312·3) calculated: 42·31% C, 6·46% H; found: 42·1% C, 6·53% H.

The authors wish to thank Mr G. Košický and Mr K. Paule for measuring the optical rotations and performing the analyses, respectively.

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Translated by Z. Votický.