

Synthesis of models representing the β -ether type linkage between lignin and hemicelluloses

R. BREŽNÝ and P. KOVÁČ

*Institute of Chemistry, Slovak Academy of Sciences,
809 33 Bratislava*

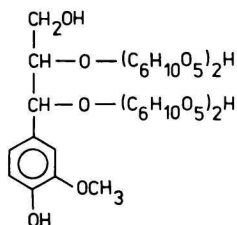
Received 2 April 1979

A series of models representing the hypothetical β -ether type linkage between lignin and hemicelluloses has been synthesized by boron trifluoride etherate-catalyzed phenacylation of methyl di-*O*-acetyl- β -D-xylopyranosides with 3,4-dimethoxy- and 4-acetoxy-3-methoxydiazoacetophenone. The formed methyl di-*O*-acetyl-*O*-(3,4-dimethoxyphenacyl)- and methyl di-*O*-acetyl-*O*-(4-acetoxy-3-methoxyphenacyl)- β -D-xylopyranosides (~20%), and the unaltered substrates (~50%) were isolated by chromatography. The target products, 2-(3,4-dimethoxyphenyl)- and 2-(4-hydroxy-3-methoxyphenyl)-2-hydroxyethyl ethers, were obtained by subsequent deacetylation and reduction.

Описывается синтез ряда соединений моделирующих гипотетическую β -эфирную связь между лигнином и гемицеллюлозами. Исходные метил-ди-*O*-ацетил- β -D-ксилопиранозиды были этерифицированы с 3,4-диметокси- и 4-ацетокси-3-метоксидиазоацетофенонами с эфиратом трехфтористого бора в качестве катализатора. Образовавшиеся метил-*O*-(3,4-диметоксифенацил)- или метил-*O*-(4-ацетокси-3-метоксифенацил)-ди-*O*-ацетил- β -D-ксилопиранозиды (~20%) и непрореагировавший субстрат (~50%) были разделены хроматографически. Требуемые 2-(3,4-диметоксифенил)- и 2-(4-гидрокси-3-метоксифенил)-2-гидроксиэтилэфир были приготовлены деацетилированием и восстановлением.

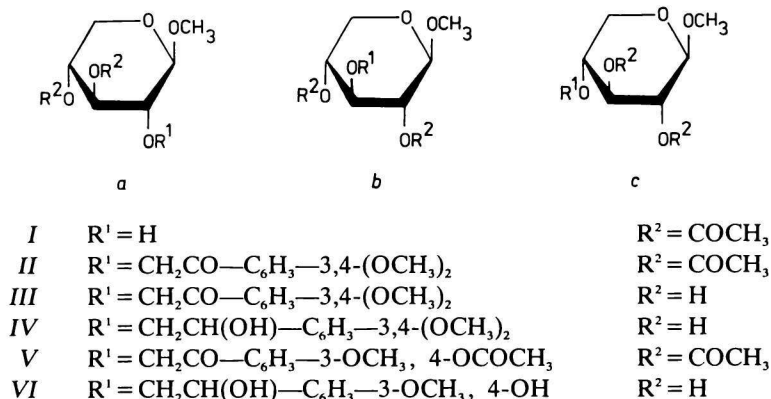
During model experiments aimed at the clarification of the nature and the mode of the formation of lignin—carbohydrate linkages *Freudenberg* and *Harkin* [1] have isolated, from an “in vitro” dehydrogenation of coniferyl alcohol in a saturated solution of sucrose, a product to which they ascribed the following structure (see the formula on p. 137).

One of the sucrose residues attached to arylpropane unit was easily removable by acid hydrolysis strongly indicating the presence of the expected benzyl ether linkage. Since the linkage to guaiacylpropane of the other sucrose residue was not acid-labile, one of its possible formulations is the proposed β -ether type linkage.



The presence of acid-stable lignin—carbohydrate linkages in materials isolated from plants has been demonstrated [2, 3] but the lack of information on their nature makes it impossible as yet to confirm or reject the existence of the β -ether type lignin—carbohydrate linkages in wood.

The object of the present work was the synthesis of 3,4-dimethoxyphenacyl ethers (*IIIa—c*), and β -guaiacyl- and β -veratrylglycol ethers (*IVa—c* and *VIa—c*) of methyl β -D-xylopyranoside (Scheme 1), models for detailed studies of the chemical properties of the β -ether type linkage between lignin and hemicelluloses.



Scheme 1

On account of their structural features favourable for reactivity in S_N reactions the readily obtainable phenacyl halides may appear to be good alkylating agents for alcohols as they are for phenols, carboxylic acids, amines or water. Nevertheless, syntheses of phenacyl ethers by etherification has been described only with lower aliphatic alcohols. In the presence of stronger bases necessary for increasing the nucleophilicity of alcohols phenacyl halides show a pronounced tendency to Favorsky rearrangement and other unwanted conversions [4]. Therefore, as a recourse, rather than using phenacyl halides in the presence of a base, phenacyl ethers of lower alcohols were prepared using as alkylating agents

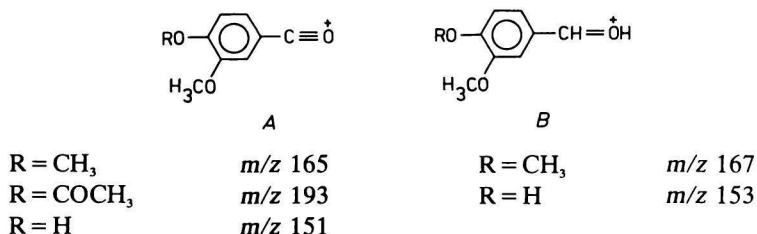
diazoacetophenones and an acid catalyst. In these conversions [5], analogously to diazoalkylation known not to cause migration of acyl groups [6], the competing decomposition of diazoketones was minimized by using a large excess of the alcoholic component, which was then conveniently disposed of by distillation. When more precious or nonvolatile alcohols are to be phenacylated in this way the key task is to promote the interaction of the diazoketone with the alcohol on one hand, and on the other to minimize the decomposition of the reagent in the presence of the acid catalyst. As we have found, this situation can be achieved primarily by proper adjustment of the concentration of the reacting components; in our experiments variations of such parameters as the temperature or the catalyst (e.g. aluminium chloride in place of boron trifluoride etherate) had little effect upon the outcome of the reaction. Phenacylation of di-*O*-acetates *Ia*—*c* made the main progress, as shown by t.l.c., by the addition of the first portions of the reagent to the solution of the whole amount of the sugar derivative and the catalyst. Further additions of diazoketone were progressively less effective and the amount over 2 equivalents was useless as then it contributed more to the contamination of the reaction mixture than to the progress of phenacylation. Moisture is another factor responsible for lowering the yield of the wanted products. Diazoketones hydrolyze easily and the reaction mixtures contained invariably substances (most probably α -hydroxyketones and/or bis-phenacyl ethers) indistinguishable according to t.l.c. from products formed in blank experiments using water as the hydroxylic component.

The reaction of methyl di-*O*-acetyl- β -*D*-xylopyranosides with the used diazoacetophenones gave only low yields ($\sim 20\%$) of the desired products which could not be obtained pure without resorting to chromatography. Since most of the by-products present in the reaction mixtures show higher chromatographic mobility than both the wanted phenacyl ethers and the starting di-*O*-acetates, the products of the decomposition of the diazoketones can be readily removed and about 50% of the unaltered starting material can be recovered.

Deacetylation of methyl di-*O*-acetyl- β -*D*-xylopyranoside 3,4-dimethoxyphenacyl ethers (*IIa*—*c*) was smoothly effected with a catalytic amount of sodium methoxide in methanol. Subsequent reduction of the products with sodium borohydride gave high yields of the target methyl β -*D*-xylopyranoside β -veratrylglycol ethers. On the other hand, deacetylation with sodium methoxide in methanol in the *Va*—*c* series was not a clean reaction. The reaction, with simultaneous reduction of the carbonyl group, can be easily done with lithium aluminium hydride. In view of the further use of β -veratryl- and β -guaiacylglycol ethers (*IVa*—*c* and *VIa*—*c*) as models for lignin—carbohydrate linkages no attempts were made to resolve the possible pairs of the formed diastereoisomers and at the determination of their absolute configuration.

The mass spectra of compounds in the series *II*—*VI* contained noticeable

molecular ion peaks at m/z 426, 342, 344, 454, and 330 but no significant differences in the fragmentation of the positional isomers could be found. The presence of the phenacyl group was manifested by a characteristic [7] fragment A ($R = \text{CH}_3$ for *Ia*—*c* and *IIIa*—*c*; $R = \text{OCOCH}_3$ and/or $R = \text{H}$ for *Va*—*c*) present in the spectra. The volatility of the substances diminishes by reduction of the phenacyl group. As a result, in addition to the characteristic fragment B (Scheme 2) ($R = \text{CH}_3$ for *IVa*—*c*; $R = \text{H}$ for *VIa*—*c*) the mass spectra contained



Scheme 2

peaks (m/z 312, 298, and 280) indicating partial pyrolysis of the substances under the conditions of the measurements.

Experimental

Melting points were determined on a Kofler hot-stage. Optical rotations were measured with a Perkin—Elmer, Model 141 automatic polarimeter. Mass spectra (70 eV) were obtained at an emission of 300 μA using a Jeol 100D instrument. Thin-layer chromatography (t.l.c.) was performed on Silica gel G-coated glass slides. Detection was effected by spraying with 5% (v/v) sulfuric acid in ethanol and heating until permanent char spots were visible. Preparative chromatography was carried out on columns of dry-packed Silica gel 60 (Merck, Darmstadt). Boron trifluoride etherate was distilled from calcium hydride under diminished pressure. The series of partially acetylated methyl β -D-xylopyranosides (*Ia*—*c*) was prepared as described [8—10]. Physical constants of the prepared substances are given in Table 1.

3,4-Dimethoxy- and 4-acetoxy-3-methoxydiazoacetophenone

Veratroyl chloride (5.4 g; 0.03 mol, [11]) or acetylvanilloyl chloride (6.9 g; 0.03 mol, [12]) in dichloromethane (10 ml) was added at -10°C with stirring to a solution of diazomethane (from *N*-nitrosomethyl urea, 10 g, 0.1 mol) in dichloromethane (150 ml). Cooling was removed and the mixture was stirred until t.l.c. showed that the reaction was complete (~ 1 h). One spot (R_f 0.63 and 0.66, respectively) was detected using chloroform—acetone 10 : 1 as the mobile phase. The solution was concentrated to give solid

Table 1
Characteristics of the prepared substances

| Compound | Formula | M | Calculated/found | | M.p. °C | [α] _D (°) | R _t | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|----------|---|--------|------------------|------|------------------------|----------------------------------|---------------------------------------|------|--|--------|-------|------|------------------------|----------------|---------------------------------------|-------|------|------|--|--------|-------|------|-------------|----------------|---------------------------------------|-------|------|------|--|--------|-------|------|-------------|----------------|-------------------|-------|------|------|--|--------|-------|------|-------------|----------------|-------------------|-------|------|------|--|--------|-------|------|-------------|----------------|-------------------|-------|------|-----|--|--------|-------|------|----------|---|-------------------|-------|------|-----|--|--|-------|------|----------|---|-------------------|-------|------|-----|--|--|-------|
| | | | % C | % H | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| IIa | C ₂₀ H ₂₆ O ₁₀ | 426.41 | 56.33 | 6.15 | — | −3.6 (c 1.01) | 0.60 ^a , 0.39 ^b | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | 56.20 | 6.11 | | | | IIb | | | 56.33 | 6.15 | 112.5—114 ^c | −45.0 (c 0.99) | 0.60 ^a , 0.39 ^b | 56.26 | 6.12 | IIc | | | 56.33 | 6.15 | — | −28.8 (c 0.66) | 0.60 ^a , 0.39 ^b | 56.26 | 6.10 | IIIa | C ₁₆ H ₂₂ O ₈ | 342.34 | 56.13 | 6.48 | 160.5—162.5 | +20.8 (c 1.05) | 0.13 ^a | 55.80 | 6.56 | IIIb | | | 56.13 | 6.48 | 179 —181.5 | −72.6 (c 1.00) | 0.18 ^a | 56.10 | 6.44 | IIIc | | | 56.13 | 6.48 | 130.5—131.5 | −64.3 (c 0.95) | 0.11 ^a | 56.05 | 6.41 | IVa | C ₁₆ H ₂₄ O ₈ | 344.35 | 55.80 | 7.02 | 175 —177 | — | 0.51 ^c | 55.73 | 6.98 | IVb | | | 55.80 | 7.02 | 149 —152 | — | 0.57 ^c | 55.70 | 6.99 | IVc | | | 55.80 |
| IIb | | | 56.33 | 6.15 | 112.5—114 ^c | −45.0 (c 0.99) | 0.60 ^a , 0.39 ^b | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | 56.26 | 6.12 | | | | IIc | | | 56.33 | 6.15 | — | −28.8 (c 0.66) | 0.60 ^a , 0.39 ^b | 56.26 | 6.10 | IIIa | C ₁₆ H ₂₂ O ₈ | 342.34 | 56.13 | 6.48 | 160.5—162.5 | +20.8 (c 1.05) | 0.13 ^a | 55.80 | 6.56 | IIIb | | | 56.13 | 6.48 | 179 —181.5 | −72.6 (c 1.00) | 0.18 ^a | 56.10 | 6.44 | IIIc | | | 56.13 | 6.48 | 130.5—131.5 | −64.3 (c 0.95) | 0.11 ^a | 56.05 | 6.41 | IVa | C ₁₆ H ₂₄ O ₈ | 344.35 | 55.80 | 7.02 | 175 —177 | — | 0.51 ^c | 55.73 | 6.98 | IVb | | | 55.80 | 7.02 | 149 —152 | — | 0.57 ^c | 55.70 | 6.99 | IVc | | | 55.80 | 7.02 | — | — | 0.50 ^c | 55.61 | 7.13 | | | | |
| IIc | | | 56.33 | 6.15 | — | −28.8 (c 0.66) | 0.60 ^a , 0.39 ^b | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | 56.26 | 6.10 | | | | IIIa | C ₁₆ H ₂₂ O ₈ | 342.34 | 56.13 | 6.48 | 160.5—162.5 | +20.8 (c 1.05) | 0.13 ^a | 55.80 | 6.56 | IIIb | | | 56.13 | 6.48 | 179 —181.5 | −72.6 (c 1.00) | 0.18 ^a | 56.10 | 6.44 | IIIc | | | 56.13 | 6.48 | 130.5—131.5 | −64.3 (c 0.95) | 0.11 ^a | 56.05 | 6.41 | IVa | C ₁₆ H ₂₄ O ₈ | 344.35 | 55.80 | 7.02 | 175 —177 | — | 0.51 ^c | 55.73 | 6.98 | IVb | | | 55.80 | 7.02 | 149 —152 | — | 0.57 ^c | 55.70 | 6.99 | IVc | | | 55.80 | 7.02 | — | — | 0.50 ^c | 55.61 | 7.13 | | | | | | | | | | | | | | |
| IIIa | C ₁₆ H ₂₂ O ₈ | 342.34 | 56.13 | 6.48 | 160.5—162.5 | +20.8 (c 1.05) | 0.13 ^a | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | 55.80 | 6.56 | | | | IIIb | | | 56.13 | 6.48 | 179 —181.5 | −72.6 (c 1.00) | 0.18 ^a | 56.10 | 6.44 | IIIc | | | 56.13 | 6.48 | 130.5—131.5 | −64.3 (c 0.95) | 0.11 ^a | 56.05 | 6.41 | IVa | C ₁₆ H ₂₄ O ₈ | 344.35 | 55.80 | 7.02 | 175 —177 | — | 0.51 ^c | 55.73 | 6.98 | IVb | | | 55.80 | 7.02 | 149 —152 | — | 0.57 ^c | 55.70 | 6.99 | IVc | | | 55.80 | 7.02 | — | — | 0.50 ^c | 55.61 | 7.13 | | | | | | | | | | | | | | | | | | | | | | | | |
| IIIb | | | 56.13 | 6.48 | 179 —181.5 | −72.6 (c 1.00) | 0.18 ^a | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | 56.10 | 6.44 | | | | IIIc | | | 56.13 | 6.48 | 130.5—131.5 | −64.3 (c 0.95) | 0.11 ^a | 56.05 | 6.41 | IVa | C ₁₆ H ₂₄ O ₈ | 344.35 | 55.80 | 7.02 | 175 —177 | — | 0.51 ^c | 55.73 | 6.98 | IVb | | | 55.80 | 7.02 | 149 —152 | — | 0.57 ^c | 55.70 | 6.99 | IVc | | | 55.80 | 7.02 | — | — | 0.50 ^c | 55.61 | 7.13 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| IIIc | | | 56.13 | 6.48 | 130.5—131.5 | −64.3 (c 0.95) | 0.11 ^a | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | 56.05 | 6.41 | | | | IVa | C ₁₆ H ₂₄ O ₈ | 344.35 | 55.80 | 7.02 | 175 —177 | — | 0.51 ^c | 55.73 | 6.98 | IVb | | | 55.80 | 7.02 | 149 —152 | — | 0.57 ^c | 55.70 | 6.99 | IVc | | | 55.80 | 7.02 | — | — | 0.50 ^c | 55.61 | 7.13 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| IVa | C ₁₆ H ₂₄ O ₈ | 344.35 | 55.80 | 7.02 | 175 —177 | — | 0.51 ^c | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | 55.73 | 6.98 | | | | IVb | | | 55.80 | 7.02 | 149 —152 | — | 0.57 ^c | 55.70 | 6.99 | IVc | | | 55.80 | 7.02 | — | — | 0.50 ^c | 55.61 | 7.13 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| IVb | | | 55.80 | 7.02 | 149 —152 | — | 0.57 ^c | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | 55.70 | 6.99 | | | | IVc | | | 55.80 | 7.02 | — | — | 0.50 ^c | 55.61 | 7.13 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| IVc | | | 55.80 | 7.02 | — | — | 0.50 ^c | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | 55.61 | 7.13 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

Table 1 (Continued)

| Compound | Formula | <i>M</i> | Calculated/found | | M.p. °C | [α] _D (°) | <i>R_f</i> |
|------------|----------------------|----------|------------------|------|-------------------------|----------------------------------|---------------------------------------|
| | | | % C | % H | | | |
| <i>Va</i> | $C_{21}H_{26}O_{11}$ | 454.42 | 55.50 | 5.77 | — | -5.6 (<i>c</i> 1.00) | 0.64 ^a , 0.52 ^b |
| | | | 55.41 | 5.68 | | | |
| <i>Vb</i> | | | 55.50 | 5.77 | — | -36.6 (<i>c</i> 1.8) | 0.63 ^a , 0.51 ^b |
| | | | 55.47 | 5.69 | | | |
| <i>Vc</i> | | | 55.50 | 5.77 | — | -28.8 (<i>c</i> 0.75) | 0.63 ^a , 0.52 ^b |
| | | | 55.36 | 5.71 | | | |
| | | | | | | | |
| <i>VIa</i> | $C_{15}H_{22}O_8$ | 330.33 | 54.54 | 6.71 | 171 —173.5 ^d | — | 0.39 ^e |
| | | | 54.41 | 6.76 | | | |
| <i>VIb</i> | | | 54.54 | 6.71 | 176 —180 | — | 0.41 ^e |
| | | | 54.30 | 6.86 | | | |
| <i>VIc</i> | | | 54.54 | 6.71 | — | — | 0.40 ^e |
| | | | 54.40 | 6.63 | | | |

a) Chloroform:acetone 10:1; *b*) benzene:ethylacetate 2:1; *c*) chloroform:methanol 10:1; *d*) crystallized from acetone—ether; *e*) crystallized from ethanol—isopropyl ether.

residue. Crystallization (with substantial losses) from isopropyl ether gave material melting at 71—73°C (decomp.) and 93—95°C (decomp.), respectively. In the reactions described below no differences were observed by t.l.c. between reactions performed with crystallized and crude products.

*Methyl di-O-acetyl-O-3,4-dimethoxyphenacyl- (IIa—c) and
-O-4-acetoxy-3-methoxyphenacyl-β-D-xylopyranosides (Va—c)*

The respective diazoketone (1.7 or 1.9 g; 0.008 mol) in dichloromethane (19 ml) was added with stirring at 0°C to a mixture of methyl di-O-acetyl-β-D-xylopyranoside (*Ia—c*) (1 g; 0.004 mol), drierite (1.5 g), and boron trifluoride etherate (0.4 ml) in dichloromethane (7.5 ml) at a rate assuring reasonable evolution of nitrogen. When the addition was complete (~15 min) the mixture was stirred for additional 5 min, filtered and the filtrate was washed with a saturated solution of sodium hydrogen carbonate, water, dried and concentrated. Chromatography of the residue using benzene—ethyl acetate (4 : 1 or 9 : 2) gave 350—370 mg (20.6—21.8%) or 360—380 mg (19.8—20.9%) of the corresponding phenacyl ethers (*II* or *V*).

Methyl O-dimethoxyphenacyl-β-D-xylopyranosides (IIIa—c)

Methanolic 1 M sodium methoxide (0.5 ml) was added to the solution of any of the foregoing compounds (200 mg; 0.5 mmol) in dry methanol (30 ml) and the mixture was left at room temperature until t.l.c. showed that the reaction was complete (2—3 h). The solution was treated with Dowex 50 W (H⁺ form) resin, filtered, concentrated and the residue was crystallized from ethyl acetate. Yield ~135 mg, 84%.

*Methyl O-[2-(3,4-dimethoxyphenyl)-2-hydroxyethyl]-β-D-
-xylopyranosides (IVa—c)*

Sodium borohydride (35 mg; 0.9 mmol) was added at 0°C to a solution of the phenacyl ether (*IIIa—c*) (100 mg; 0.3 mmol) in 1,2-dimethoxyethane (3 ml). When the reaction was complete, as shown by t.l.c. (1 1/2 h), methanol (10 ml) was added and the mixture was treated with Dowex 50 W (H⁺ form) resin. After filtration and several concentrations with methanol the products were obtained (90—100 mg) in virtually quantitative yields. Compounds *IVa* and *IVb* were crystallized from ethyl acetate.

*Methyl O-[2-(4-hydroxy-3-methoxyphenyl)-2-hydroxyethyl]-β-D-
-xylopyranosides (VIa—c)*

Lithium aluminium hydride (100 mg; 2.6 mmol) was added to a solution of compounds *Va—c* (120 mg; 0.26 mmol) in dry tetrahydrofuran (3 ml), and the mixture was stirred at room temperature for 3 h. T.l.c. showed then that the deacetylation and reduction were complete, and the excess of the reagent was destroyed with a little aqueous tetrahydrofuran. The mixture was neutralized with dilute acetic acid, filtered and the insoluble material was washed several times with tetrahydrofuran. Column chromatography with

chloroform—methanol (20 : 1) gave 60—65 mg (83—89%) of a chromatographically homogeneous sirup. Compounds *Via* and *Vib* were crystallized from ethyl acetate.

Acknowledgements. The authors thank V. Kováčik and V. Mihálov for mass spectrometry and G. Košický for optical rotation measurements.

References

1. Freudenberg, K. and Harkin, J. M., *Chem. Ber.* 93, 2814 (1960).
2. Pew, J. C. and Weyna, P., *Tappi* 45, 247 (1962).
3. Efendieva, N. F., *Khim. Drev.* 1977, 51.
4. Kende, A. S., *Org. Reactions* 11, 261 (1960).
5. Newman, M. S. and Beal, P. F., *J. Amer. Chem. Soc.* 72, 5161 (1950).
6. Mastronardi, I. O., Flematti, S. M., Deferrari, J. O., and Gros, E. G., *Carbohydr. Res.* 3, 177 (1966).
7. Kováčik, V., Škamla, J., Joniak, D., and Košíková, B., *Chem. Ber.* 102, 1513 (1969).
8. Kováč, P. and Palovčík, R., *Chem. Zvesti* 31, 98 (1977).
9. Kováč, P. and Alföldi, J., *Chem. Zvesti* 32, 519 (1978).
10. Kováč, P. and Alföldi, J., *Chem. Zvesti* 33, 785 (1979).
11. *Beilsteins Handbuch der organischen Chemie*, 4th Ed., H X 397.
12. Rosenmund, K. W. and Letzsche, F., *Chem. Ber.* 56, 1481 (1923).

Translated by P. Kováč